The Danish Pesticide Leaching Assessment Programme

Monitoring results 1999–June 2012

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Preface

In 1998, the Danish Parliament initiated the Danish Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The Danish Government funded the first phase of the programme from 1998 to 2001. The programme has now been prolonged twice, initially with funding from the Ministry of the Environment and the Ministry of Food, Agriculture and Fisheries for the period 2002 to 2009, and presently with funding from the Danish Environmental Protection Agency for the period 2010 to 2015.

The work was conducted by the Geological Survey of Denmark and Greenland (GEUS), the Department of Agroecology (AGRO) at Aarhus University and the Department of Bioscience (BIOS) also at Aarhus University, under the direction of a management group comprising Walter Brüsch (GEUS), Annette E. Rosenbom (GEUS), Lis Wollesen de Jonge (AGRO), Preben Olsen (AGRO), Carsten Brian Nielsen, (BIOS) and Steen Marcher (Danish Environmental Protection Agency).

Lea Frimann Hansen (Danish Environmental Protection Agency) is chairman of the steering group, and the members are Steen Marcher (Danish Environmental Protection Agency), Flemming Larsen (GEUS), Walter Brüsch (GEUS), Erik Steen Kristensen (AGRO) and Christian Kjær (BIOS).

This report presents the results for the period May 1999–June 2012. Results covering part of the period May 1999–June 2011 have been reported previously (Kjær *et al.*, 2002, Kjær *et al.*, 2003, Kjær *et al.*, 2004, Kjær *et al.*, 2005c, Kjær *et al.*, 2006, Kjær *et al.*, 2007, Kjær *et al.*, 2008, Kjær *et al.*, 2009, Rosenbom *et al.*, 2010b, Kjær *et al.*, 2011 and Brüsch *et al.*, 2013). The present report should therefore be seen as a continuation of previous reports with the main focus on the leaching risk of pesticides applied during the monitoring period 2010-2012.

The report was prepared jointly by Walter Brüsch, Annette E. Rosenbom, René K. Juhler and Lasse Gudmundsson (all GEUS), Preben Olsen and Finn Plauborg (AGRO), and Carsten B. Nielsen (BIOS). While all authors contributed to the whole report, authors were responsible for separate aspects as follows:

- Pesticide and bromide leaching: Preben Olsen, Annette E. Rosenbom and Walter Brüsch.
- Soil water dynamics and water balances: Annette E. Rosenbom, Finn Plauborg and Carsten B. Nielsen.
- Pesticide analysis quality assurance: René K. Juhler.

Walter Brüsch
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Summary

In 1998, the Danish Parliament initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The objective of the PLAP is to improve the scientific foundation for decision-making in the Danish regulation of pesticides. The specific aim is to analyse whether pesticides applied in accordance with current regulations leach to groundwater in unacceptable concentrations. The programme currently evaluates the leaching risk of 50 pesticides and 50 degradation products at five agricultural sites ranging in size from 1.2 to 2.4 ha. The evaluation is based upon monitoring results representing detections in 1 meters depth (water collected via drains and suction cups) and detections in groundwater monitoring screens (1.5-4.5 meter below ground surface, hereafter m b.g.s.).

This report presents the results for the monitoring period June 2010–June 2012. Results covering the period May 1999–June 2010 have been reported previously (Kjær *et al.*, 2002, Kjær *et al.*, 2003, Kjær *et al.*, 2004, Kjær *et al.*, 2005c, Kjær *et al.*, 2007, Kjær *et al.*, 2008, Kjær *et al.*, 2009, Rosenbom *et al.*, 2010b, Kjær *et al.*, 2011 and Brüsch *et al.*, 2013). The present report should therefore be seen as a continuation of previous reports with the main focus on the leaching risk of pesticides applied during 2010-12.

In the period 2010-2012, 24 pesticides were applied and monitored, and in total 43 pesticides and degradation products were investigated. In the monitoring year 2011/12 10 pesticides were applied and monitored.

Highlights from the **monitoring period June 2010-July 2012:**

- Metalaxyl-M was found in soil water in low concentrations in the unsaturated zone. However, two degradation products (CGA 62826 and CGA 108906) were leached from the root zone in average concentrations exceeding 0.1 µg/L, and in the second monitoring year in high concentrations >0.1 µg/L. Leaching was most pronounced in the suctions cups, where both compounds were found 1 m b.g.s. in concentrations up to 4.8 µg/L. CGA 108906 was found in Tylstrup in 95% of the analysed groundwater samples and in 32% of the analysed samples the concentration exceeded 0.1 µg/L. The degradation products were present in the groundwater before metalaxyl-M was applied, and the background concentration of the degradation products makes it difficult to determine whether the elevated concentrations observed in monitoring wells are due to the metalaxyl-M applied in 2010 or partly to previous applications occurring at the "upstream" neighbouring fields. As a consequence of the monitoring results, the Danish Environmental Protection Agency (EPA) has withdrawn the approval of metalaxyl-M per 1. August 2013.

- Bifenox-acid (degradation product of bifenox) can on loamy soil leach through the root zone and enter both the drainage water system and groundwater monitoring wells in high concentrations >0.1 µg/L. Average concentration in the drainage water exceeded 0.1 µg/L and concentrations exceeding 0.1 µg/L were observed up to 12 months after application at Silstrup, but in this monitoring year the concentrations

often are <0.1 μg/L. In Estrup and Faardrup the leaching has nearly stopped in 2011/12. The degradation product nitrofen was found in drain water in low in concentrations <0.1 μg/L but nitrofen has been found in concentration up to 0.34 μg/L in few samples drain water from Silstrup. As a consequence of the monitoring results EPA has withdrawn the approval of bifenox in August 2012.

- Leaching of TFMP, a metabolite of fluazifop-P-butyl, used in a new admissible dose that is 50% lower than in past applications, was negligible in 2010-2011. When, in the past (before the imposed regulation), fluazifop-P-butyl was used at a much higher dose, TMFP leaching above 0.1 μg/L to both drains and groundwater monitoring wells was observed. In the end of the monitoring year 2011/2012 concentrations of TFMP > 0.1 μg/L was measured in drain and wells at Silstrup after application in April 2012. The leaching is probably caused by a quick preferential flow. EPA has evaluated that the average concentration is below 0.1 μg/L per year. TFMP will be monitored carefully in the future.

- Glyphosate and its degradation product AMPA, have been found frequently in low concentrations in the drain water at Estrup, and in few samples from Faardrup. In the drain water from Estrup, glyphosate concentrations up to 10 μg/L have been found, and at Estrup glyphosate was found in two ground water samples below 0.1 μg/L. AMPA was found more frequently but only in the drain water in concentrations up to 0.58 μg/L.

- Aclonifen, boscalid and cyafamid and metabolites did not leach from the root zone during the monitoring period. Diflufenican and the break down product AE-B107137 were found in few drain water samples, while AE-05422291 did not leach. The degradation product thiacloprid amid, from the parent thiacloprid, was measured in one sample while the parent was not detected.

The results of the **entire monitoring period 1999-2012** covering **50** pesticides show that:

- Of the 50 pesticides applied, 16 pesticides and/or their degradation product(s) (aclonifen, aminopyralid, boscalid, clopyralid, chlormequat, cyazofamid, desmedipham, fenpropimorph, florasulam, iodosulfuron-methyl-natrium, linuron, mesotrione, thiacloprid, thiamethoxam, tribenuron-methyl and triasulfuron) did not leach during the entire monitoring period.

- The monitoring data indicate pronounced leaching of 16 of the applied pesticides and/or their degradation products. The following compounds leached through the soil entering drains and suction cups (placed 1 m b.g.s.) in average concentrations exceeding 0.1 μg/L:

  o *azoxystrobin* and its degradation product *CyPM*
  o *bentazone*
  o *CL153815* (degradation product of picolinafen)
  o *diflufenican (AE-B107103)*
  o *pirimicarb-desmethyl-formamido* (degradation product of pirimicarb)
  o *propyzamide*
  o *tebuconazole*

- o *glyphosate* and its degradation product *AMPA*
- o **CGA 108906 and CGA 62826** (degradation products of metalaxyl-M)
- o **PPU** (degradation products of rimsulfuron)
- o **bifenox-acid** (degradation product of bifenox)
- o **ethofumesate**
- o **TFMP** (degradation product of fluazifop-P-butyl)
- o *metamitron* and its degradation product **desamino-metamitron**
- o **desamino-diketo-metribuzin** and **diketo-metribuzin** (degradation products of metribuzin)
- o **terbuthylazine** and its degradation products: **desethyl-terbuthylazine**, *2-hydroxy-desethyl-terbuthylazine* and *hydroxy-terbuthylazine.*

For pesticides and/or their degradation products *marked in italics*, pronounced leaching is mainly confined to the depth of 1 m b.g.s., where pesticides were frequently found in samples collected from drains and suction cups, while a limited number of detections (fewer than 5 samples per field) exceeding 0.1 µg/L were found in groundwater monitoring wells.

For the pesticides and/or their degradation products **marked in bold**, pronounced leaching below the depth of 1 m b.g.s. was observed. Apart from PPU, these were all frequently detected in concentrations exceeding 0.1 µg/L in groundwater monitoring wells with exceedance of 0.1 µg/L observed more than six months after application.

- PPU was in 2011/12 found in most samples in concentrations <0.1 µg/L and only few concentrations exceeding 0.1 µg/L. Elevated concentrations just below 0.1 µg/L were found in groundwater monitoring wells during the monitoring period, thus confirming the pronounced leaching and high persistency of PPU in soil and groundwater. As a consequence of the monitoring results EPA has withdrawn the approval of rimsulfuron.

- The monitoring data also indicate leaching of an additional 18 pesticides, but in low concentrations. Although concentrations exceeded 0.1 µg/L in several water samples collected from suction cups and drains (1 m b.g.s.), average leaching concentrations on a yearly basis did not exceed 0.1µ/L. None of the compounds were found in groundwater monitoring wells in concentrations exceeding 0.1 µg/L.

In order to describe soil and groundwater transport, a bromide tracer was applied to the fields. Bromide and pesticide concentrations are measured monthly in both the unsaturated and the saturated zones, and weekly in the drainage water. This report covers the period May 1999–June 2012 and presents the monitoring results from the five agricultural sites presently monitored. The main focus is on evaluating the leaching risk of the pesticides applied during 2010-2012.

Dansk sammendrag

I 1998 vedtog Folketinget at iværksætte projektet "Varslingssystem for udvaskning af Pesticider til grundvandet" (VAP). VAP er et omfattende moniteringsprogram, der undersøger udvaskning af pesticider anvendt i landbrug under reelle markforhold. Programmet har til formål at undersøge, om godkendte pesticider eller deres nedbrydningsprodukter – ved regelret brug og dosering – udvaskes til grundvandet i koncentrationer over grænseværdien for herigennem at udvide det videnskabelige grundlag for danske myndigheders (Miljøstyrelsen) procedurer for regulering af godkendte sprøjtemidler. Udvaskningsrisikoen for 50 pesticider samt 50 nedbrydnings-produkter er således op til i dag undersøgt på fem marker, der har en størrelse på mellem 1,2 og 2,4 ha. Undersøgelsen bygger på moniteringsresultater henholdsvis repræsenterende fund i en meters dybde (indhentet via dræn og sugeceller) og fund i grundvandsmoniteringsfiltre (1.5-4.5 meter under terræn, herefter m.u.t.).

Denne rapport opsummerer analyseresultaterne for de stoffer, der har indgået i moniteringsperioden fra juni 2010 til juni 2012, og analyseresultater af stoffer der har været moniteret i denne periode og tidligere. Resultater fra de foregående år, fra maj 1999 til juni 2010, er afrapporteret i tidligere rapporter.

I perioden 2010-2012 blev der udbragt og moniteret 24 pesticider på de fem VAP-marker. I alt 30 pesticider og nedbrydningsprodukter blev undersøgt. Medtages pesticider udbragt før 2010, er der undersøgt 43 stoffer i denne periode.

I juni 2011 til juni 2012 blev der udbragt 10 pesticider, og 18 pesticider og nedbrydningsprodukter blev analyseret.

"Highlights" fra den seneste **moniteringsperiode 2010-2012** viser følgende:

- Metalaxyl-M blev fundet i små koncentrationer i den umættede zone, <0,05 μg/l, men to nedbrydningsprodukter (CGA 62826 og CGA 108906) blev i 2010/11 og 2011/12 udvasket fra rodzonen i høje koncentrationer, der ofte overskred 0,1 μg/l. Begge stoffer blev fundet i sugeceller placeret 1 m.u.t. i højere koncentrationer i andet moniteringsår end i året før (maksimum koncentration 4,8 μg/l). CGA 108906 blev i 2010-12 i Tylstrup fundet i ca. 95% af de analyserede grundvandsprøver. I 32% af prøverne var koncentrationerne større end 0,1 μg/l. Nedbrydnings-produkterne var til stede i grundvandet opstrøms marken før sprøjtningen med metalaxyl-M, hvilket gør det vanskeligt at skelne mellem indflydelsen fra sidste og tidligere sprøjtninger på nabomarker. Som følge af moniteringsresultaterne blev godkendelserne af metalaxyl-M tilbagekaldt fra markedet pr. 1. august 2013.

- Bifenox-syre (nedbrydningsprodukt af bifenox, senest udbragt foråret 2011) på lerjorde udvaskes fortsat fra rodzonen til både dræn og grundvandsfiltre i koncentrationer over 0,1 μg/l i vandprøver udtaget fra Silstrup, men i modsætning til tidligere oftere i koncentrationer < 0,1 μg/L. I Estrup og Fårdrup findes stoffer stort set ikke i moniteringsåret. Nedbrydningsproduktet nitrofen blev fundet i drænvand i relativt små koncentrationer under 0,1 μg/L, men stoffet er dog i enkelte tilfælde fundet i koncentrationer op til 0,34 μg/l i drænprøver fra Silstrup. Som følge af de

første års resultater blev godkendelsen af bifenox trukket tilbage i august 2012, og stoffet er ikke længere på det danske marked.

- Efter fluazifop-P-butyl blev anvendt i foråret 2011 i en ny 50% reduceret dosis, var udvaskningen af nedbrydningsproduktet TMFP ganske lille, hvilket er i modsætning til tidligere, hvor der blev observeret udvaskning der overskred 0,1 µg/l ved anvendelse af den højere dosis. I slutningen af moniteringsåret blev der dog fundet TMFP i koncentrationer $\geq$ 0,1 µg/L i dræn og grundvandsboringer efter at moderstoffet var blevet udbragt i april 2012 på Silstrup. Da nedbrydningsproduktet således ved den nye lave dosis kan overskride grænseværdien f.eks. ved hurtig transport gennem sprækker og makroporer, har Miljøstyrelsen indhentet yderligere moniteringsresultater fra Silstrup. På baggrund af disse data har Miljøstyrelsen vurderet, at den årlige gennemsnitskoncentration ikke overskrider 0,1 µg/L. Stoffet følges stadig nøje.

- Glyphosat og nedbrydningsproduktet AMPA er gennem 2010-2012 fundet hyppigt i lave koncentrationer i dræn i Estrup og få gange i Fårdrup. I Estrup er der fundet glyphosat i dræn i koncentrationer op til 10 µg/l, mens stoffet alene er fundet under grænseværdien i to grundvandsprøver. AMPA er fundet lidt hyppigere, men kun i drænvand, hvor den maksimale koncentration var 0,58 µg/l.

- Aclonifen, boscalid og cyazofamid blev ikke udvasket i moniteringsperioden. Udvaskningen af bentazon var på niveau med tidligere målinger, der var ikke overskridelser af grænseværdien i grundvandsprøverne. Diflufenican og nedbrydningsproduktet AE-B107137 blev fundet i enkelte drænprøver, mens AE-05422291 ikke blev fundet. Nedbrydningsproduktet thiacloprid-amid fra thiacloprid blev fundet i en enkelt prøve, mens moderstoffet og thiacloprid-sulfonsyre ikke blev påvist.

Resultater for **hele moniteringsperioden 1999-2012**, som omfatter 50 pesticider viser følgende:

- Af de 50 pesticider der er blevet udbragt, blev 16 pesticider eller nedbrydnings-produkter heraf (aclonifen, aminopyralid, boscalid, clopyralid, chlormequat, cyazofamid, desmedipham, fenpropimorph, florasulam, iodosulfuron-methyl-natrium, linuron, mesotrion, thiacloprid, thiamethoxam, tribenuron-methyl og triasulfuron) ikke fundet udvasket til jord- og grundvand i løbet af den samlede moniteringsperiode.

- 16 udbragte stoffer eller nedbrydningsprodukter fra disse gav anledning til en udvaskning gennem rodzonen til dræn og sugeceller, beliggende i ca. 1 m.u.t. i gennemsnitskoncentrationer over 0,1 µg/l og til sugeceller i samme dybde i tilsvarende koncentrationer:

  - *azoxystrobin* og dets nedbrydningsprodukt *CyPM*
  - *bentazon*
  - *CL153815* (nedbrydningsprodukt af picolinafen)
  - *Diflufenican (AE-B107103)*
  - *pirimicarb-desmethyl-formamido* (nedbrydningsprodukt af pirimicarb)
  - *propyzamid*

- o *tebuconazol*
- o *glyphosat* og dets nedbrydningsprodukt *AMPA*
- o **CGA 108906 og CGA 62826** (nedbrydningsprodukt af metalaxyl-M)
- o **PPU** (nedbrydningsprodukt af rimsulfuron)
- o **bifenox-syre** (nedbrydningsprodukt af bifenox)
- o **ethofumesat**
- o **TFMP** (nedbrydningsprodukt af fluazifop-P-butyl)
- o *metamitron* og dets nedbrydningsprodukt d**esamino-metamitron**
- o **desamino-diketo-metribuzin** og **diketo-metribuzin**
  (nedbrydningsprodukter af metribuzin)
- o **terbuthylazin** og dets nedbrydningsprodukter **desethyl-terbuthylazin**,
  2-hydroxy-desethyl-terbuthylazin og 2-hydroxy-terbuthylazin.

For de pesticider eller nedbrydningsprodukter der er *fremhævet med kursiv* var udvaskningen primært begrænset til 1 m.u.t., hvor de blev fundet hyppigt i dræn og sugeceller. Selvom hovedparten af stofferne blev fundet i koncentrationer over 0,1 µg/l i grundvandsfiltrene, var antallet af overskridelser få (mindre end 5 pr. mark).

Pesticider **markeret med fed** blev dog udvasket til grundvandsfiltrene i en grad, så Miljøstyrelsen har foretaget nye vurderinger med forbud eller anden regulering af anvendelsen til følge.

- På nær PPU blev samtlige stoffer relativt hyppigt fundet i koncentrationer over 0,1 µg/l i grundvandsfiltre, hvor koncentrationer over 0,1 µg/l blev fundet mere end seks måneder efter udbringning. PPU er dog i 2011/12 fundet en del gange i Jyndevad og Tylstrup, men kun relativt få prøver (10 prøver) fra Jyndevad indeholdt mere end 0,1 µg/l PPU. De 10 prøver med fund over grænseværdien stammer fra 6 sugeceller og fra 4 grundvandsprøver. Miljøstyrelsen har trukket godkendelsen tilbage, fordi de foreliggende data tyder på, at PPU er persistent, og fordi resultaterne fra VAP ikke umiddelbart kan "frikende" PPU.

- Andre 18 stoffer gav anledning til mindre udvaskning. Selv om flere af disse stoffer i 1 m.u.t. ofte blev fundet i koncentrationer over 0,1 µg/l, var der ikke tale om, at udvaskningen som årsgennemsnit oversteg 0,1 µg/l. Stofferne blev heller ikke fundet i grundvandsfiltrene i koncentration over 0,1 µg/l, tabel 8.1 og 8.3.

Bromid er anvendt som sporstof for at beskrive vandtransporten. Bromid- og pesticidkoncentrationer bliver analyseret månedligt i vandprøver udtaget i den umættede og mættede zone, og ugentligt i prøver af drænvand. I denne rapport præsenteres moniteringsresultaterne for de fem områder for perioden fra maj 1999 til juni 2012 primært med fokus på pesticider udbragt i 2010-2012.

1 Introduction

There is growing public concern in Denmark about pesticide contamination of our surface waters and groundwater. Pesticides and their degradation products have increasingly been detected in groundwater during the past decade and are now present in much of the Danish groundwater. Under the Danish National Groundwater Monitoring Programme (GRUMO), pesticides have so far been detected in 52% of all screens monitored and in 60% of the screens placed in the upper shallow groundwater (Thorling, L. (red), 2011).

The detection of pesticides in groundwater over the past 20 years has given rise to the desire to enhance the scientific foundation for the existing approval procedure for pesticides and to improve the present risk assessment tools. A main issue in this respect is that the EU assessment, and hence also the Danish assessment of the risk of pesticide leaching to groundwater, is largely based on data from modelling, laboratory or lysimeter studies. However, these types of data may not adequately describe the leaching that may occur under actual field conditions. Although models are widely used within the registration process, their validation requires further work, not least because of the limited availability of field data (Boesten, 2000). Moreover, laboratory and lysimeter studies do not include the spatial variability of the soil parameters (hydraulic, chemical, physical and microbiological soil properties) affecting pesticide leaching. This is of particular importance for silty and loamy soils, where preferential transport may have a major impact on pesticide leaching. In fact, various field studies suggest that considerable preferential transport of several pesticides occurs to a depth of 1 m under conditions comparable to those pertaining in Denmark (Kördel, 1997, Jacobsen & Kjær, 2007).

The inclusion of field studies, i.e. test plots exceeding 1 ha, in risk assessment of pesticide leaching to groundwater is considered an important improvement to the risk assessment procedures. For example, the US Environmental Protection Agency (US-EPA) has included field-scale studies in its risk assessments since 1987. Pesticides that may potentially leach to the groundwater are required to be included in field studies as part of the registration procedure. The US-EPA has therefore conducted field studies on more than 50 pesticides (US Environmental Protection Agency, 1998). A similar concept has also been adopted within the European Union (EU), where Directive 91/414/EEC, Annexe VI (Council Directive 97/57/EC of 22 September 1997) enables field leaching study results to be included in the risk assessments.

1.1 Objective

In 1998, the Danish Government initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme with the purpose of evaluating the leaching risk of pesticides under field conditions. The PLAP is intended to serve as an early warning system providing decision-makers with advance warning if approved pesticides leach in unacceptable concentrations. The programme focuses on pesticides

used in arable farming and PLAP monitors leaching at five agricultural test sites representative of Danish conditions.

The objective of the PLAP is to improve the scientific foundation for decision-making in the Danish registration and approval procedures for pesticides, enabling field studies to be included in risk assessment of selected pesticides. The specific aim is to analyse whether pesticides applied in accordance with current regulations leach at levels exceeding the maximum allowable concentration of 0.1 µg/L.

1.2 Structure of the PLAP

The pesticides included in the PLAP were selected by the Danish Environmental Protection Agency on the basis of expert judgement. At present, 50 pesticides and 50 degradation products have been included in the PLAP. All the compounds analysed are listed in Appendix 1.
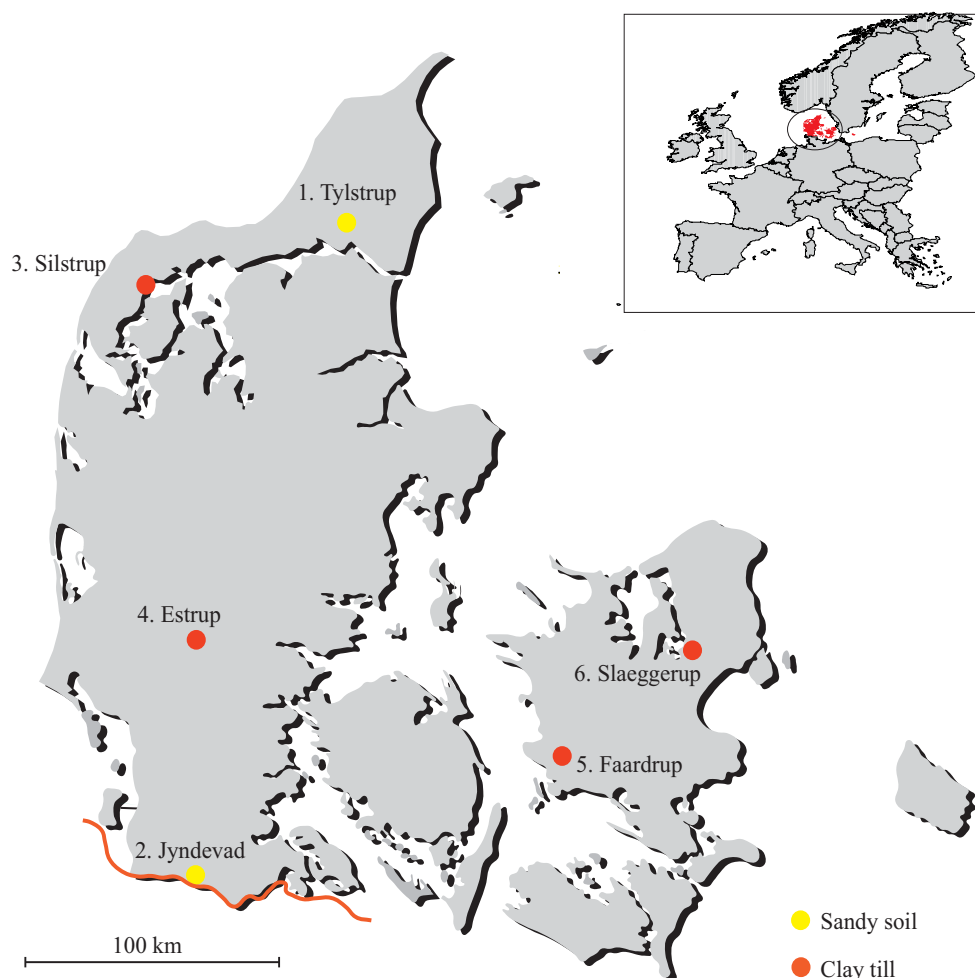
Figure 1.1. Location of the PLAP sites **Tylstrup**, **Jyndevad**, **Silstrup**, **Estrup** and **Faardrup**. Monitoring at Slaeggerup was terminated on 1 July 2003.

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Soil type and climatic conditions are considered to be some of the most important parameters controlling pesticide leaching. The PLAP initially encompassed six test sites representative of the dominant soil types and the climatic conditions in Denmark (Figure 1.1).

Monitoring at the Slaeggerup site was terminated on 1 July 2003, and results from that site are not included in the present report. For the monitoring results from this site see Kjær *et al.* (2003). The groundwater table at all the sites is shallow, thereby enabling pesticide leaching to groundwater to be rapidly detected (Table 1.1). Cultivation of the PLAP sites is in line with conventional agricultural practice in the vicinity. The pesticides are applied at maximum permitted doses and in the manner specified in the regulations. Hence any pesticides or degradation products appearing in the groundwater downstream of the sites can be related to the current approval conditions pertaining to the individual pesticides. The five test sites encompassed by the present report were selected and established during 1999. Monitoring was initiated at Tylstrup, Jyndevad and Faardrup in 1999 and at Silstrup and Estrup in 2000 (Table 1.1).

Table 1.1. Characteristics of the five PLAP sites (modified from Lindhardt *et al.,* 2001).

	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
Location	Brønderslev	Tinglev	Thisted	Askov	Slagelse
Precipitation[1] (mm/y)	668	858	866	862	558
Pot. evapotransp.[1] (mm/y)	552	555	564	543	585
W x L (m)	70 x 166	135 x 184	91 x 185	105 x 120	150 x 160
Area (ha)	1.1	2.4	1.7	1.3	2.3
Tile drain	No	No	Yes	Yes	Yes
Depths to tile drain (m b.g.s.)			1.1	1.1	1.2
Monitoring initiated	May 1999	Sep 1999	Apr 2000	Apr 2000	Sep 1999
Geological characteristics					
– Deposited by	Saltwater	Meltwater	Glacier	Glacier/meltwater	Glacier
– Sediment type	Fine sand	Coarse sand	Clayey till	Clayey till	Clayey till
– DGU symbol	YS	TS	ML	ML	ML
– Depth to the calcareous matrix (m b.g.s.)	6	5–9	1.3	1–4[2]	1.5
– Depth to the reduced matrix (m b.g.s.)	>12	10–12	5	>5[2]	4.2
– Max. fracture depth[3] (m)	–	–	4	>6.5	8
– Fracture intensity 3–4 m depth (fractures/m)	–	–	<1	11	4
– Ks in C horizon (m/s)	$2.0 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$3.4 \cdot 10^{-6}$	$8.0 \cdot 10^{-8}$	$7.2 \cdot 10^{-6}$
Topsoil characteristics					
– DK classification	JB2	JB1	JB7	JB5/6	JB5/6
– Classification	Loamy sand	Sand	Sandy clay loam/ sandy loam	Sandy loam	Sandy loam
– Clay content (%)	6	5	18–26	10–20	14–15
– Silt content (%)	13	4	27	20–27	25
– Sand content (%)	78	88	8	50–65	57
– pH	4–4.5	5.6–6.2	6.7–7	6.5–7.8	6.4–6.6
– TOC (%)	2.0	1.8	2.2	1.7–7.3	1.4

[1] *Yearly normal based on a time series for the period 1961–90. The data refer to precipitation measured 1.5 m above ground.*
[2] *Large variation within the field.*
[3] *Maximum fracture depth refers to the maximum fracture depth found in excavations and wells.*

Site characterization and monitoring design are described in detail in Lindhardt *et al.* (2001). The present report presents the results of the monitoring period May 1999–June 2012. The main focus of this report is on the leaching risk of pesticides applied during 2010-12. For a detailed description of the earlier part of the monitoring period (May 1999–June 2009), see previous publications on http://pesticidvarsling.dk/publ_result-/index.html. Under the PLAP the leaching risk of pesticides is evaluated on the basis of at least two years of monitoring data.

For some pesticides the present report must be considered preliminary because they have been monitored for an insufficient length of time.

Hydrological modelling of the unsaturated zone at each PLAP site supports the monitoring data. The MACRO model (version 5.1), see Larsbo *et al.* (2005), was used to describe the soil water dynamics at each site during the entire monitoring period from May 1999–June 2012. The five site models have been calibrated for the monitoring period May 1999–June 2004 and validated for the monitoring period July 2004–June 2012.

Scientifically valid methods of analysis are essential to ensure the integrity of the PLAP. The field monitoring work has therefore been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. The quality assurance methodology and results are presented in Section 7.

2 Pesticide leaching at Tylstrup

2.1 Materials and methods

2.1.1 Site description and monitoring design

Tylstrup is located in northern Jutland (Figure 1.1). The test field covers a cultivated area of 1.2 ha (70 m x 166 m) and is practically flat, with windbreaks bordering the eastern and western sides. Based on two soil profiles dug in the buffer zone around the test field the soil was classified as a Humic Psammentic Dystrudept (Soil Survey Staff, 1999). The topsoil is characterised as loamy sand with 6% clay and 2.0% total organic carbon (Table 1.1). The aquifer material consists of an approx. 20 m deep layer of marine sand sediment deposited in the Yoldia Sea. The southern part is rather homogeneous, consisting entirely of fine-grained sand, whereas the northern part is more heterogeneous due to the intrusion of several silt and clay lenses (Lindhardt *et al.,* 2001). The overall direction of groundwater flow is towards the west (Figure 2.1). During the monitoring period the groundwater table was 2.6–4.5 m b.g.s. (Figure 2.2). A brief description of the sampling procedure is provided in Appendix 2 and the analysis methods in Kjær *et al.* (2002). The monitoring design and test site are described in detail in Lindhardt *et al.* (2001). In September 2011, the monitoring system was extended with three horizontal screens (H1) 4.5 m b.g.s. in the South-Eastern corner of the field (Figure 2.1). A brief description of the drilling and design of H1 is given in Appendix 8.
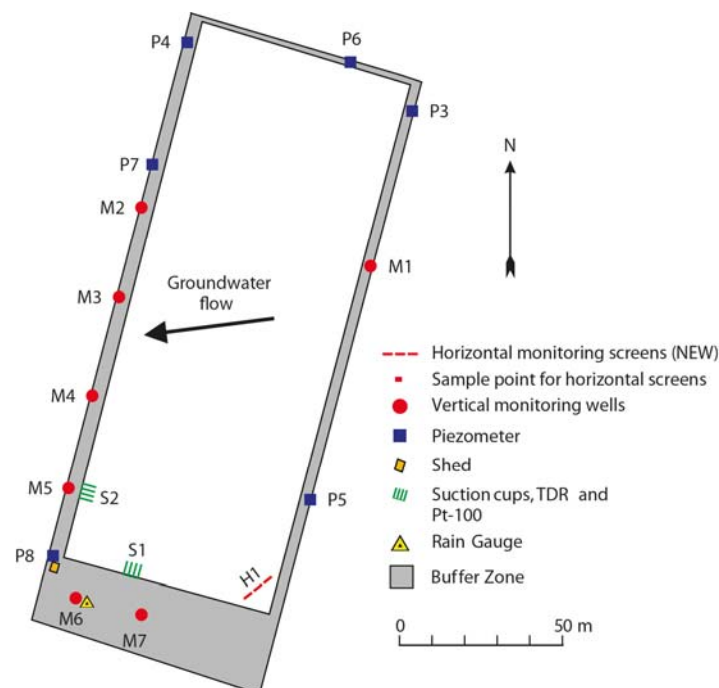
Figure 2.1. Overview of the **Tylstrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted monthly and half-yearly from suction cups and selected both vertical and horizontal monitoring screens as described in Table A2.1 in Appendix 2.

2.1.2 Agricultural management

Management practice during the 2010-12 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.1). For information about management practice during the previous monitoring periods, see previous monitoring reports available on http://pesticidvarsling.dk/publ_result/index.html.

The field was ploughed on 17 April 2011 and the field sown with spring barley (cv. TamTam) on the 19. April which emerged on 24 April. A spraying with the herbicides ioxynil and bromoxynil was done 10 May, the substances was however not included in the monitoring. Spraying of fungi was done on 20. June using boscalid and epoxiconazol, of which only boscalid was monitored. At harvest 16. August, the yields of grain amounted to 75.7 hkg/ha (85% dry matter) and on the 18 august 34.6 hkg of straw (100% dry matter) was removed from the field. Grain yield was well above the average for the soil type and year (Plantedirektoratet. 2011). Ploughing of the field was done 22 March 2012 and 2 days later the field was sown with spring barley (cv. TamTam).

2.1.3 Model setup and calibration

The numerical model MACRO (version 5.1) was applied to the Tylstrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model was used to simulate water and bromide transport in the unsaturated zone during the full monitoring period May 1999–June 2012 and to establish an annual water balance.

Compared to Brüsch *et al.* (2013), a year of validation was added to the MACRO-setup for the Tylstrup site. The setup was hereby calibrated for the monitoring period May 1999-June 2004 and "validated" for the monitoring period July 2004-June 2012. Daily time series of groundwater table measured in the piezometers located in the buffer zone, soil water content measured at three different depths (25, 60, and 110 cm b.g.s.) from the two profiles S1 and S2 (Figure 2.1) and the bromide concentration measured in the suction cups located 1 and 2 m b.g.s. were used in the calibration and validation process. Data acquisition, model setup and results related to simulated bromide transport are described in Barlebo *et al.* (2007).

2.2 Results and discussion

2.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 2.2). The overall trends in soil water saturation were modelled successfully, with the model capturing soil water dynamics at all depths (Figure 2.2 C-E). During the last five hydraulic years the level in water saturation at 25 cm b.g.s. was, however, overestimated. Moreover the initial decrease in water saturation observed during the five summer periods at 25, 60, and 110 cm b.g.s. was less well captured.

Table 2.1. Annual water balance for **Tylstrup** (mm y^{-1}). Precipitation is corrected to soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation[2]	Precipitation	Irrigation	Actual evapotranspiration	Groundwater recharge[3]
1.5.99–30.6.99[1]	120	269	0	112	156
1.7.99–30.6.00	773	1073	33	498	608
1.7.00–30.6.01	773	914	75	487	502
1.7.01–30.6.02	773	906	80	570	416
1.7.02–30.6.03	773	918	23	502	439
1.7.03–30.6.04	773	758	0	472	287
1.7.04–30.6.05	773	854	57	477	434
1.7.05–30.6.06	773	725	67	488	304
1.7.06–30.6.07	773	1147	59	591	615
1.7.07–30.6.08	773	913	126	572	467
1.7.08–30.6.09	773	1269	26	600	695
1.7.09–30.6.10	773	867	27	424	470
1.7.10–30.6.11	773	950	57	506	501
1.7.11–30.6.12	773	923	24	501	446

[1] *Accumulated for a two-month period.*
[2] *Normal values based on time series for 1961–1990.*
[3] *Groundwater recharge is calculated as precipitation + irrigation - actual evapotranspiration.*

The dynamics of the groundwater table were well captured also the amplitude of the fluctuations, which are less well described for the previous years (Figure 2.2B).

The resulting annual water balance is shown for each hydraulic year of the monitoring period (July–June) in Table 2.1. Values for precipitation and actual evapotranspiration for the most recent hydraulic year, July 2011–June 2012, were in the middle of the range observed since monitoring began at the site, and the monthly precipitation pattern for this year was medium to high compared with earlier years, except for the driest November and Marts monitored (Appendix 4). Artificial irrigation was low compared to the other monitoring years, which could be the result of the wet period April-June. The groundwater recharge/percolation was medium compared to the other hydraulic years, and continuous (Figure 2.2B).
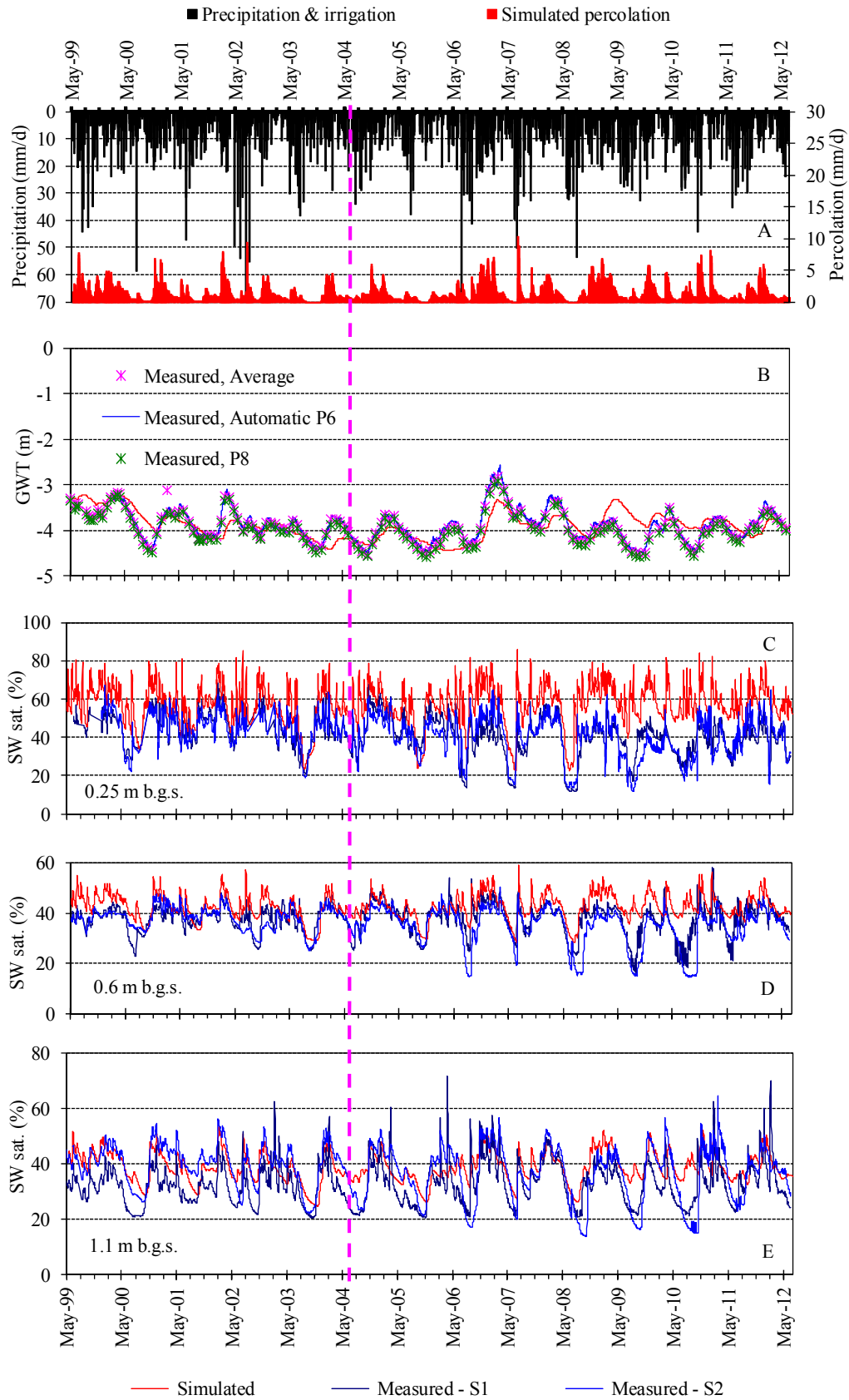
Figure 2.2. Soil water dynamics at **Tylstrup**: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in C, D, and E derive from TDR probes installed at S1 and S2 (Figure 2.1). The broken vertical line indicates the beginning of the validation period (July 2004-June 2012).

20
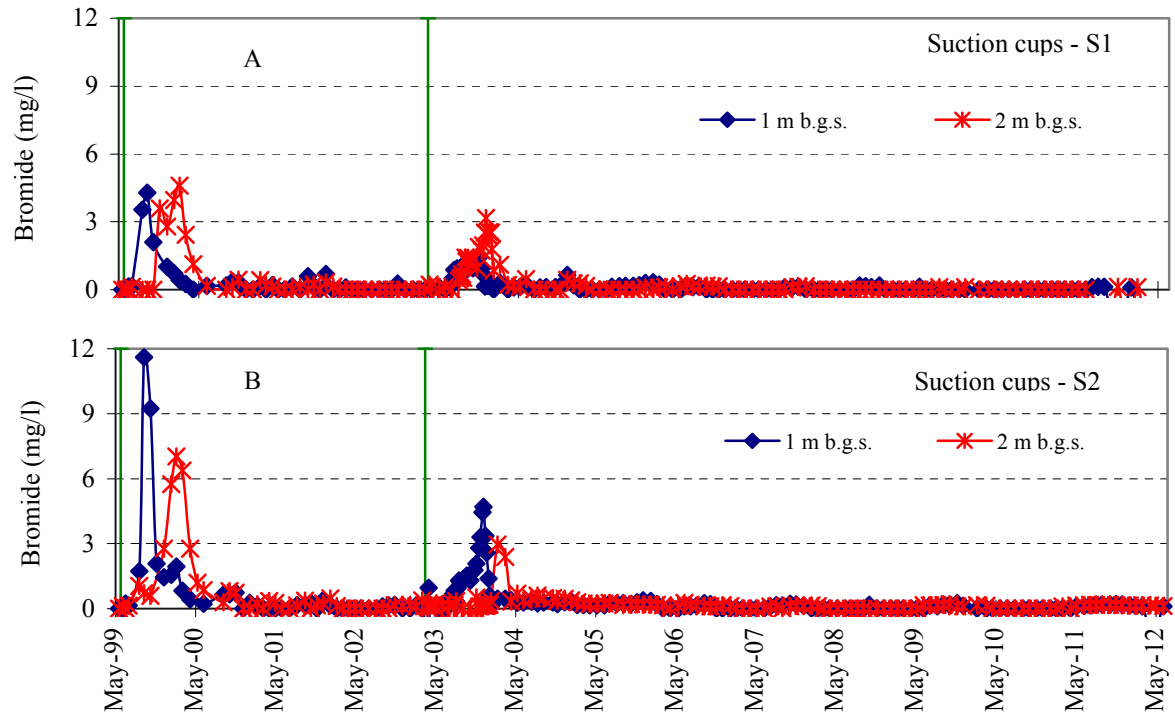
Figure 2.3. Measured bromide concentration in the unsaturated zone at **Tylstrup**. The measured data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 (A) and S2 (B) indicated in Figure 2.1. The green vertical lines indicate the dates of bromide applications.

2.2.2 Bromide leaching

Bromide has now been applied twice at Tylstrup. The bromide concentrations measured until April 2003 (Figure 2.3 and Figure 2.4) relate to the bromide applied in May 1999, as described further in Kjær *et al.* (2003). Unsaturated transport of the bromide applied in March 2003 is evaluated in Barlebo *et al.* (2007).
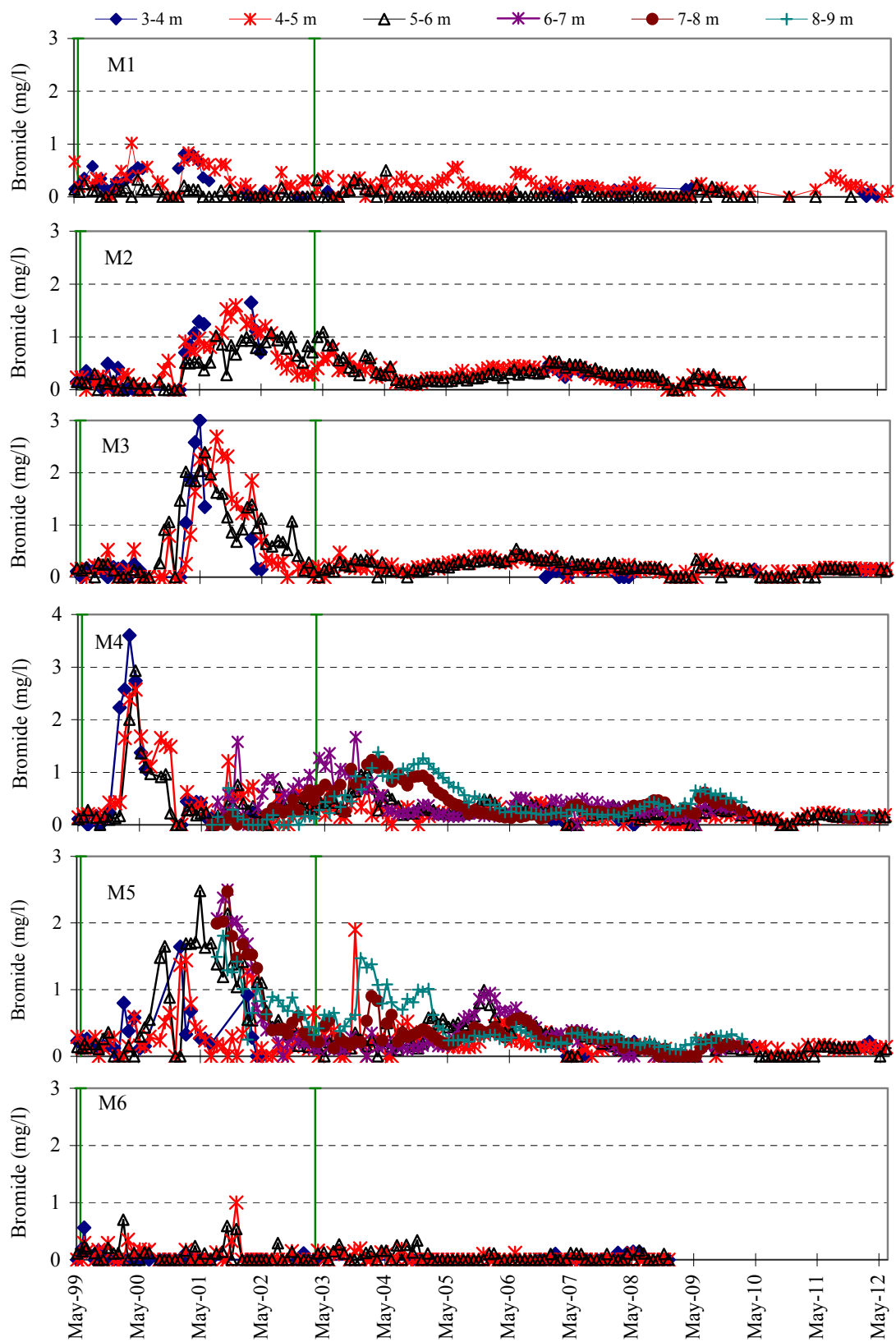
Figure 2.4. Bromide concentration in the groundwater at **Tylstrup.** The data derive from monitoring wells M1–M6. Monitoring at well M6 was suspended September 2008 (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

2.2.3 Pesticide leaching

Monitoring at Tylstrup began in May 1999 and presently encompasses several pesticides and their degradation products, as shown in Appendix 7. Pesticide applications during the latest growing seasons are listed in Table 2.2 and are shown together with precipitation and simulated precipitation in Figure 2.5.

It should be noted that precipitation in Table 2.2 is corrected to soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model. Rimsulfuron (here applied as Titus) degrade rapidly and the risk of leaching is associated with the degradation products PPU and PPU-desamino. In Table 2.2 weighted average concentrations 1 m b.g.s. (Cmean) is calculated from both S1 and S2. When these values are reported as a range it indicated that Cmean in S1 and S2 differs from each other. Pesticides applied later than April 2012 are not evaluated in this report and hence are not included in Table 2.2 and Figure 2.5.

The current report focuses on the pesticide applied from 2010 and onwards, while leaching risk of pesticides applied before 2010 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html). The leaching of rimsulfuron is further detailed in Kjær *et al.* (2005b), Rosenbom *et al.* (2009) and Rosenbom *et al.* (2010a).
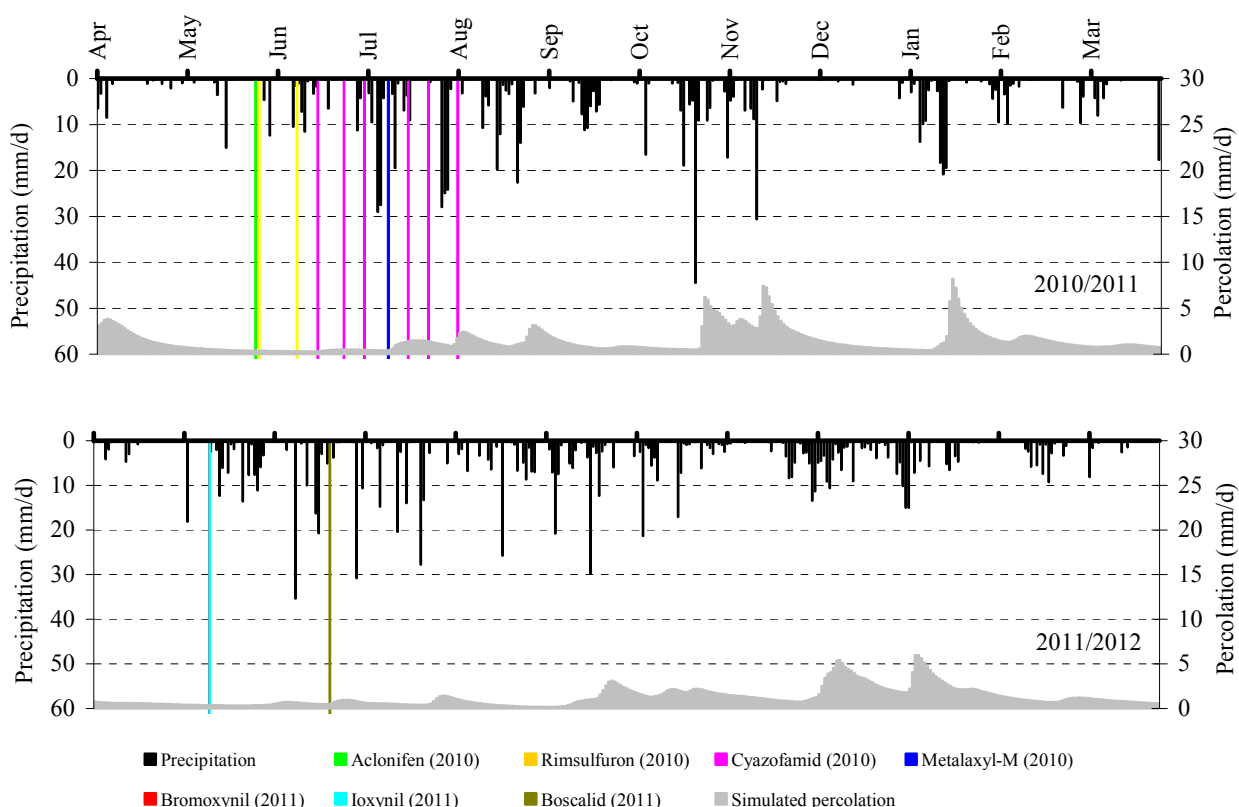
Figure 2.5. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Tylstrup** in 2010/2011 (upper) and 2011/2012 (lower). Boscalid 2011 include application boscalid and epoxyconazol.

Table 2.2. Pesticides analysed at **Tylstrup**. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Precip 1st year, Percol 1st year) and first month (Precip 1st month, Percol 1st year) after the first application C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.1) for previous applications of pesticides. (End monito) End of monitoring of pesticide or metabolite.

Crop	Applied product	Analysed pesticide	Applica. date	End monito.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol.	C_{mean}
Winter Rape 2007	CruiserRAPS	Thiamethoxam(P)	Aug 06	Apr 08	1250	700	87	57	<0.01
		CGA 322704(M)	Aug 06	Apr 08	1250	700	87	57	<0.02
	Kerb 500 SC	Propyzamide(P)	Feb 07	Apr 09	1052	472	48	40	<0.01
		RH-24580(M)	Feb 07	Apr 09	1052	472	48	40	<0.01
		RH-24644(M)	Feb 07	Apr 09	1052	472	48	40	<0.01
		RH-24655(M)	Feb 07	Apr 09	1052	472	48	40	<0.01
	Matrigon	Clopyralid(P)	Mar 07	Apr 09	1055	488	30	24	<0.02
Winter Wheat 2008	Amistar	Azoxystrobin(P)	Jun 08	Jun 11	1316	662	141	0	<0.01
		CyPM(M)	Jun 08	Jun 11	1316	662	141	0	<0.01
	Folicur EC 250	Tebuconazole(P)	Nov 07	Mar 10	1133	461	69	43	<0.01
	Stomp	Pendimethalin(P)	Oct 07	Dec 09	1032	415	36	26	<0.01
Spring Barley 2009	Amistar	Azoxystrobin(P)	Jun 09	Jun 11	909	475	138	11	<0.01
		CyPM(M)	Jun 09	Jun 11	909	475	138	11	<0.01
	Basagran M75	Bentazone(P)	May 09	Jun 12*	996	488	133	22	<0.01
Potatoes 2010	Fenix	Aclonifen(P)	May 10	Jun 12*	958	491	62	12	<0.01
	Titus WSB	PPU(M)	May 10	Jun 12*	958	491	62	12	0.01-0.02
		PPU-desamino(M)	May 10	Jun 12*	958	491	62	12	<0.01
	Ranman	Cyazofamid(P)	Jun 10	Jun 12	981	499	128	17	<0.01
	Ridomil Gold MZ Pepite	Metalaxyl-M(P)	Jul 10	Jun 12*	934	514	127	43	<0.01
		CGA 108906(M)	Jul 10	Jun 12*	934	514	127	43	0.03-0.12
		CGA 62826(M)	Jul 10	Jun 12*	934	514	127	43	<0.01-0.02
Spring Barley 2011	Bell	Boscalid (P)	Jun 10	Jun 12*	959	467	106	20	<0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
*monitoring continues the following year.

Neither aclonifen nor cyazofamid, applied on potatoes in 2010, was found in groundwater or in the unsaturated zone in 2011 or 2012.

Leaching of metalaxyl-M applied in potatoes in 2010 was minor at Tylstrup, and the compound was only detected in four samples collected from the unsaturated zone, concentration level ranging from 0.018 to 0.03 µg/L (Figure 2.6). However, two degradation products of metalaxyl-M (CGA 62826 and CGA 108906) leached from the root zone (1 m b.g.s.), the latter in average concentrations exceeding 0.1 µg/L (Table 2.2 and Figure 2.6). Both compounds were found in suction cups 1 m b.g.s. in 2010, 2011 and 2012 and the leaching of CGA 108906 had not yet ceased. CGA 108906 was analysed in 66 water samples from the unsaturated zone and CGA 108906 was fund in 76% of the samples and in 37.9% in concentrations exceeding 0.1 µg/L. The average concentration in al samples with findings was 0.437 µg/L, Table 2.3. In the second monitoring year CGA 108906 was found in even higher concentrations in the suction cups, with maximum concentrations of 2,5 and 4,8 µg/L in S1 and S2, Figure 2.6.

Table 2.3. CGA108906 analysed in the unsaturated and saturated zone, Tylstrup. Number of samples, samples with findings and samples ≥ 0.1 µg/L. Concentrations calculated by using detections.

Apr 10-Jun 12 CGA108906	Samples, number			% findings			Concentration in µg/L	
	analysed	0.02-0.1 µg/L	≥ 0.1 µg/L	0.02-0.1 µg/L	≥ 0.1 µg/L	>0.02 µg/L	average	median
unsaturated zone	66	50	25	37.9	37.9	75.8	0.437	0.109
saturated zone	131	82	42	62.6	32.1	94.7	0.126	0.067

In the saturated zone neither metalaxyl-M nor CGA 62826 was found in any samples collected from the wells situated downstream the field site before spraying, whereas both compounds were found in samples collected from M1 situated upstream of the field site (Figure 2.7). As the tracer test suggested that water sampled in M1 had not infiltrated at the PLAP site, but originated from the upstream neighbouring fields, detections in M1 show that these compound have leached from previous application occurring at these upstream neighbouring fields, where metalaxyl have also been applied (Brüsch et al 2013: Appendix 7).

In the period April 2010 to June 2012, CGA 108906 was found in 95% of analysed groundwater samples and 32% of the analysed sample concentrations exceed 0.1 µg/L. The average concentration from samples with findings is 0.13 µg/L, Table 2.3. Similar to the other compounds GCA 108906 was also detected in samples from the upstream well M1 and moreover present in the groundwater before metalaxyl-M was applied at the PLAP field in June 2010. The background concentration of CGA 108906 found in all monitoring wells makes it difficult to determine whether the elevated concentrations observed in downstream monitoring wells are due to the metalaxyl-M applied on the PLAP test site in 2010 or to previous applications on the "upstream" fields. However, the background concentration suggests that leaching of CGA 108906 occurs both from the test field as well as from neighbouring fields situated upstream our field site. Moreover, with a background level of CGA 108906 ranging between 0.02–0.3 µg/L, additional input via root zone leaching is likely to increase the frequency of exeedance of the 0.1 µg/L in samples collected from the groundwater monitoring wells.

CGA 108906 was found in concentrations up to 1,5 µg/L in downstream monitoring wells, Figure 2.7D.

Metalaxyl was on the Danish market from 1980-1995, with reported maximum allowed dosage from 1984-1995 being 375 gr. a.i./ha. It re-entered the Danish marked in 2007 as metalaxyl-M with a maximum allowed dosage of 77.6 g/ha.

Since 2006 metalaxyl-M was applied at upstream neighbouring fields where reported dosage did not exceed the maximum allowed dosage of 77.6 g a.i./ha. Usage data are not available from 1980-1995, but information from local farmers suggest that metalxyl during this period was applied on some of the upstream neighbouring fields.
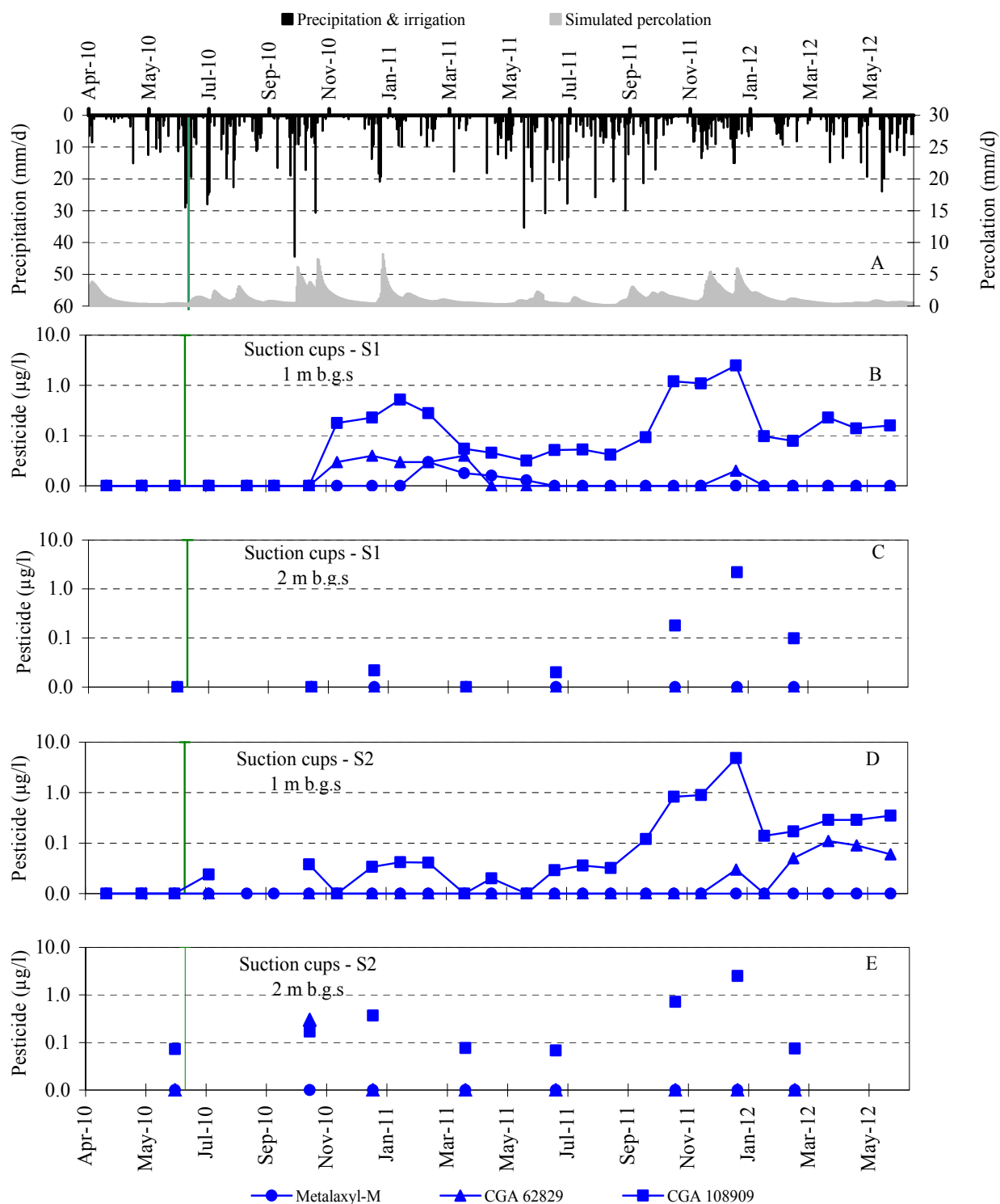
Figure 2.6. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *Metalaxyl-M, CGA 62829* and *CGA 108909* (µg/L) in suction cups installed at location S1 at 1 m b.g.s. (B) and 2 m b.g.s. (C) and location S2 at 1 m b.g.s. (D) and 2 m b.g.s. (E) at **Tylstrup**. The green vertical line indicates the date of pesticide application.
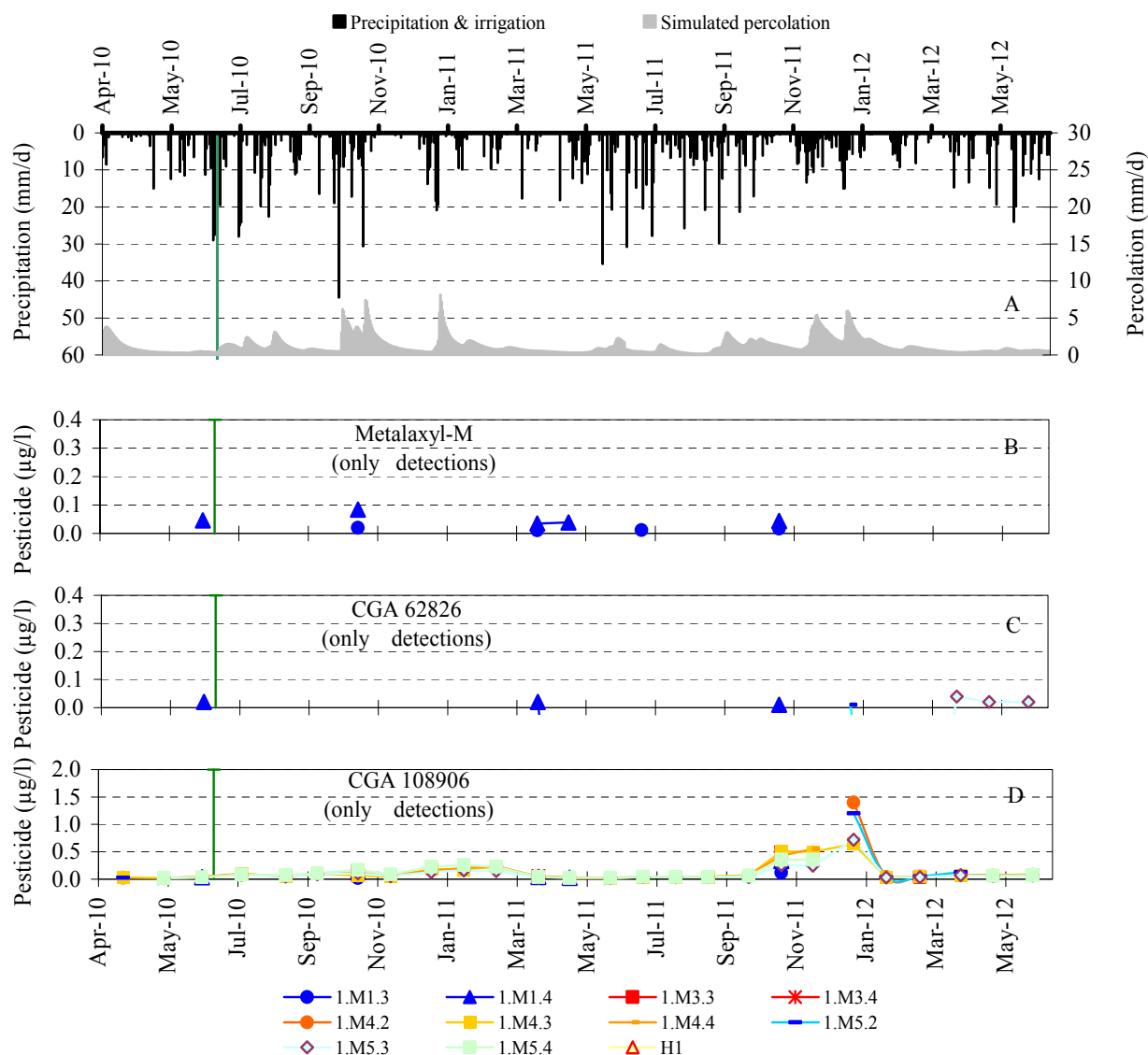
Figure 2.7. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *metalaxyl-M* (B), *CGA 62826* (C) and *CGA 108906* (D) (µg/L) in horizontal & monitoring wells at **Tylstrup**. The green vertical line indicates the date of pesticide application.

Based on available data we conclude that detected residues in the groundwater are most likely to derive from current usage of metalaxyl-M allowed since 2007 and not the initial usage allowed from 1980–1995. With an average travel time to all monitoring wells being less than 4 years (Laier et al. in prep) it is unlikely that water sampled from these screens have infiltrated the unsaturated zone before 1995. A possibility could, however, be that the residues originating from the initial usage of 375 g/ha (allowed in 1980-1995) were left in the soil and continued to leach during a long period of time. Should this be the case the persistency of these compounds would be very high allowing them to leach more than a decade after application. An assumption which do not correspond the regulatory assessment where final endpoints for DT_{50} were less than 18 days, Danish EPA (2007).

Rimsulfuron was applied on potatoes in 2010 in the same dosage as that used on potatoes in 2004. Rimsulfuron degrades rapidly in the soil, and the leaching risk is therefore associated with the degradation products PPU and PPU-desamino. At Tylstrup PPU was characterised by continuous leaching over a long period of time which has continued during the last monitoring year (June 2011 to July 2012), but in smaller concentrations. PPU was found in 83% of the samples from the unsaturated zone and in 39% of the groundwater samples, including samples from the up stream well M1. There were no findings exceeding 0.1 µg/L, (Kjær et al. 2010). The results of the 2004 application are summarized by Rosenbom *et al.* (2010a).

Boscalid was applied to spring barley in June 2011. Up to now, there have been no findings in the saturated or in the unsaturated zone in Tylstrup.

Pesticides analysed after June 2012 (aminopyralid) are not evaluated in this report.

3 Pesticide leaching at Jyndevad

3.1 Materials and methods

3.1.1 Site description and monitoring design

Jyndevad is located in southern Jutland (Figure 1.1). The test site covers a cultivated area of 2.4 ha (135 x 184 m) and is practically flat. A windbreak borders the eastern side of the test site. The area has a shallow groundwater table ranging from 1 to 3 m b.g.s. (Figure 3.2B) The overall direction of groundwater flow is towards the northwest (Figure 3.1). The soil can be classified as Arenic Eutrudept and Humic Psammentic Dystrudept (Soil Survey Staff, 1999) with coarse sand as the dominant texture class and topsoil containing 5% clay and 1.8% total organic carbon (Table 1.1). The geological description points to a rather homogeneous aquifer of meltwater sand, with local occurrences of thin clay and silt beds. A brief description of the sampling procedure is provided in Appendix 2 and the analysis methods in Kjær et al. (2002). The monitoring design and test site are described in detail in Lindhardt et al. (2001). In September 2011, the monitoring system was extended with three horizontal screens (H1) 2.5 m b.g.s. in the South-Eastern corner of the field (Figure 3.1). A brief description of the drilling and design of H1 is given in Appendix 8.

3.1.2 Agricultural management

Management practice during the 2011-12 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.2). For information about management practice during the previous monitoring periods, see previous monitoring reports available on http://pesticidvarsling.dk/publ_result/index.html.
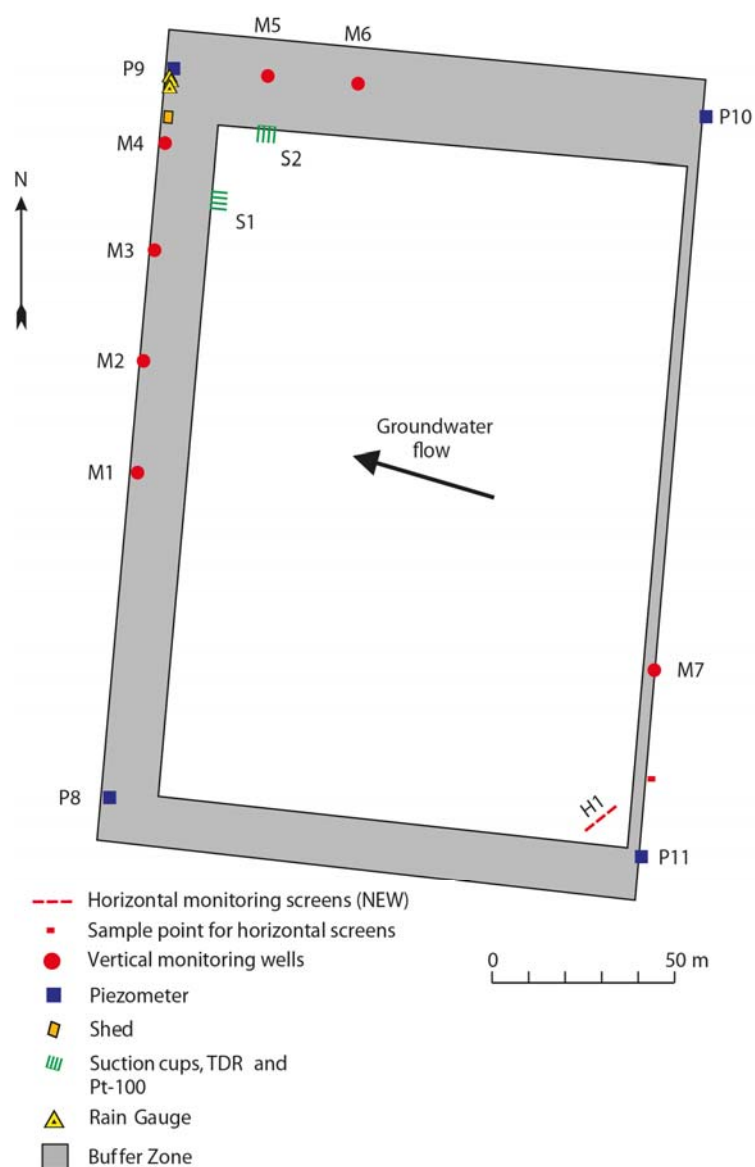
Figure 3.1. Overview of the **Jyndevad** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted monthly and half-yearly from selected horizontal and vertical monitoring screens and suctions cups as described in Table A2.1 in Appendix 2.

The field was ploughed on 22 March 2011 and the following day sown with spring barley (cv. Quench), which emerged on 5 April. Spraying of weed was done 26 April using bromoxynil, ioxynil and diflufenican of which only the later was included in the monitoring programme. Irrigation of the barley was done three times using 30 mm on 2 May, 32 mm on 23 May and 30 mm on 4 July. On 23 August the barley was harvested yielding 72.4 hkg/ha of grain (85% dry matter). Yields were significantly above the average for the year and soil type (Plantedirektoratet, 2011). An amount of 30.2 hkg/ha of straw (100% dry matter) was removed on the 25 August. Ploughing of the field was done on 30 March 2012 and sowing of maize (cv. Atrium) 3 May, emerging on 17 May.

3.1.3   Model setup and calibration

The numerical model MACRO (version 5.1, Larsbo *et al.,* 2005) was applied to the Jyndevad site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model was used to simulate water flow and bromide transport in the unsaturated zone during the full monitoring period July 1999–June 2012 and to establish an annual water balance.

Compared with the setup in Brüsch *et al.* (2013), a year of validation was added to the MACRO-setup for the Jyndevad site. The setup was hereby calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2012. For this purpose, the following time series have been used: the groundwater table measured in the piezometers located in the buffer zone, soil water content measured at three different depths (25, 60, and 110 cm b.g.s.) from the two profiles S1 and S2 (location indicated at Figure 3.1), and the bromide concentration measured in the suction cups located 1 and 2 m b.g.s.(Figure 3.3). Data acquisition, model setup as well as results related to simulated bromide transport are described in Barlebo *et al.* (2007).
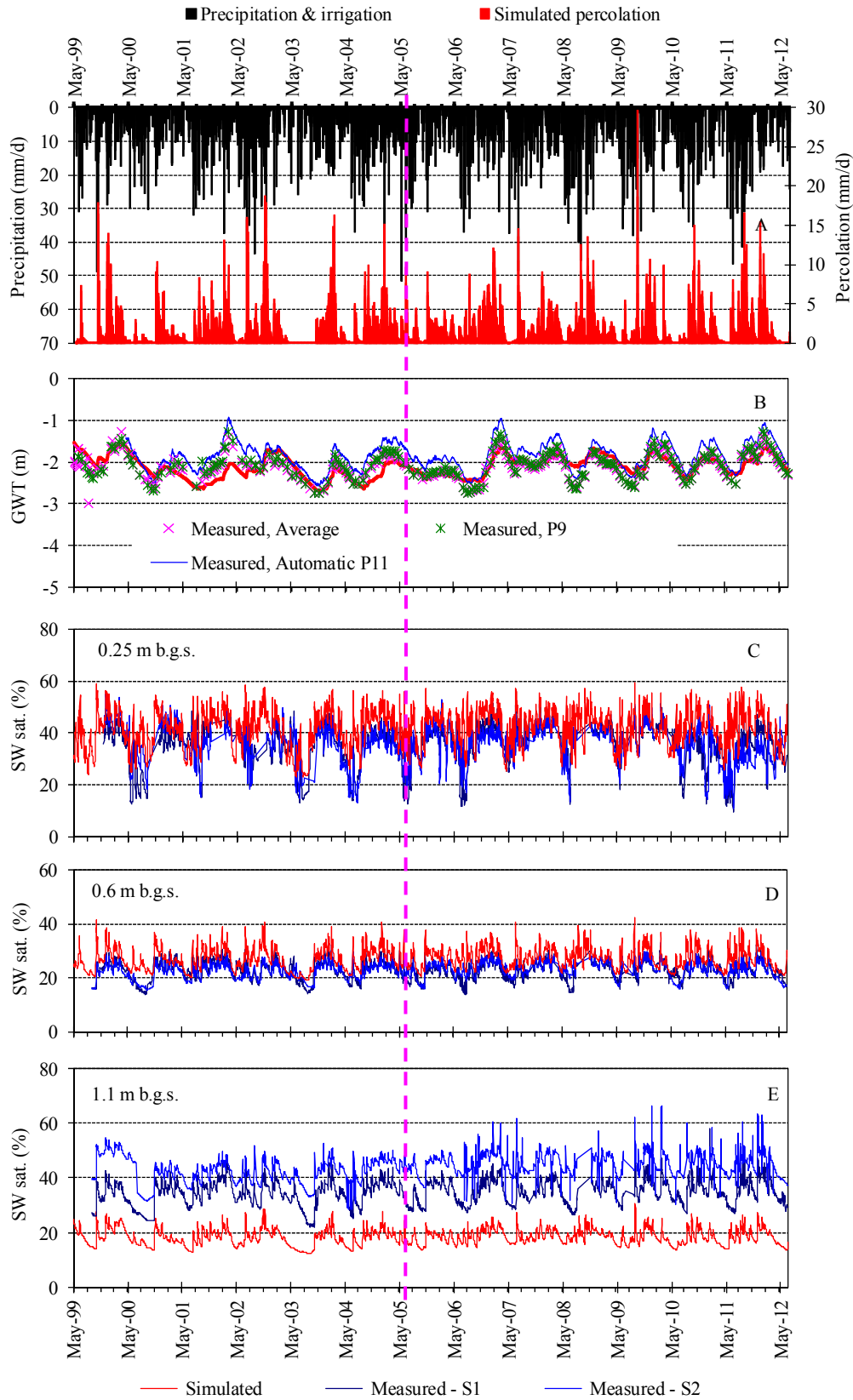
Figure 3.2. Soil water dynamics at **Jyndevad**: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D, and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in C, D, and E derive from TDR probes installed at S1 and S2 (Figure 3.1). The broken vertical line indicates the beginning of the validation period (July 2004-June 2012).

3.2 Results and discussion

3.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 3.2). The dynamics of the simulated groundwater table were well described with MACRO 5.1 (Figure 3.2B). No measurements of the water saturation were obtained during the following two periods: 1 June-25 August 2009 (given degradation in the TDR measuring system) and 7 February-6 March 2010 (given a sensor error). As noted earlier in Kjær et al. (2011), the model still had some difficulty in capturing the degree of soil water saturation 1.1 m b.g.s. (Figure 3.2E) and also the decrease in water saturation observed during summer periods at 25 and 60 cm b.g.s. A similar decrease in water saturation is observed from December 2010 to February 2011 at 25 cm b.g.s., which is caused by precipitation falling as snow (air-temperature below zero degrees Celcius). The water flow through the soil profile will hereby be delayed – a delay, which cannot be captured by the MACRO-setup.

The resulting water balance for Jyndevad for the 13 monitoring periods is shown in Table 3.1. Compared with the previous eleven years, the latest hydraulic year July 2010-June 2012 was characterised by having high precipitation, low simulated actual evapotranspiration and low irrigation values. Precipitation in the latest hydraulic year was characterised by August being the wettest, and November and Marts being the driest monitored at this site (Appendix 4). Continuous percolation 1 m b.g.s. were simulated for this hydraulic year.

Table 3.1. Annual water balance for **Jyndevad** (mm yr^{-1}). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal Precipitation[1]	Precipitation	Irrigation	Actual Evapotranspiration	Groundwater Recharge[2]
1.7.99–30.6.00	995	1073	29	500	602
1.7.00–30.6.01	995	810	0	461	349
1.7.01–30.6.02	995	1204	81	545	740
1.7.02–30.6.03	995	991	51	415	627
1.7.03–30.6.04	995	937	27	432	531
1.7.04–30.6.05	995	1218	87	578	727
1.7.05–30.6.06	995	857	117	490	484
1.7.06–30.6.07	995	1304	114	571	847
1.7.07–30.6.08	995	1023	196	613	605
1.7.08–30.6.09	995	1078	84	551	610
1.7.09–30.6.10	995	1059	80	530	610
1.7.10–30.6.11	995	1070	92	554	607
1.7.11–30.6.12	995	1159	30	488	700

[1] *Normal values based on time series for 1961-1990.*
[2] *Groundwater recharge is calculated as precipitation + irrigation - actual evapotranspiration.*
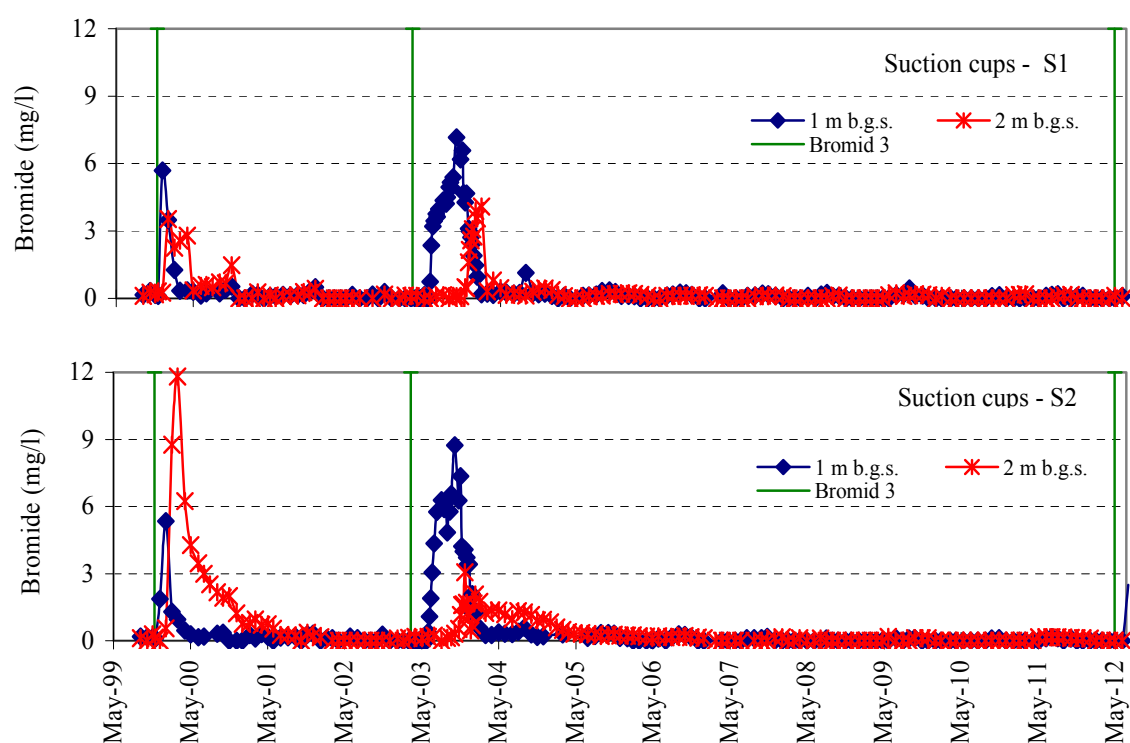
Figure 3.3. Bromide concentration in the unsaturated zone at **Jyndevad**. The measured data derive from suction cups installed 1 m b.g.s. (upper) and 2 m b.g.s. (lower) at locations S1 and S2 (Figure 3.1). The green vertical lines indicate the dates of bromide applications.

3.2.2 Bromide leaching

Bromide has now been applied twice at Jyndevad. The bromide concentrations measured until April 2003 (Figure 3.3 and Figure 3.4) relate to the bromide applied in autumn 1999, as described further in Kjær *et al.* (2003). Leaching of the bromide applied in March 2003 is evaluated in Barlebo *et al.* (2007).
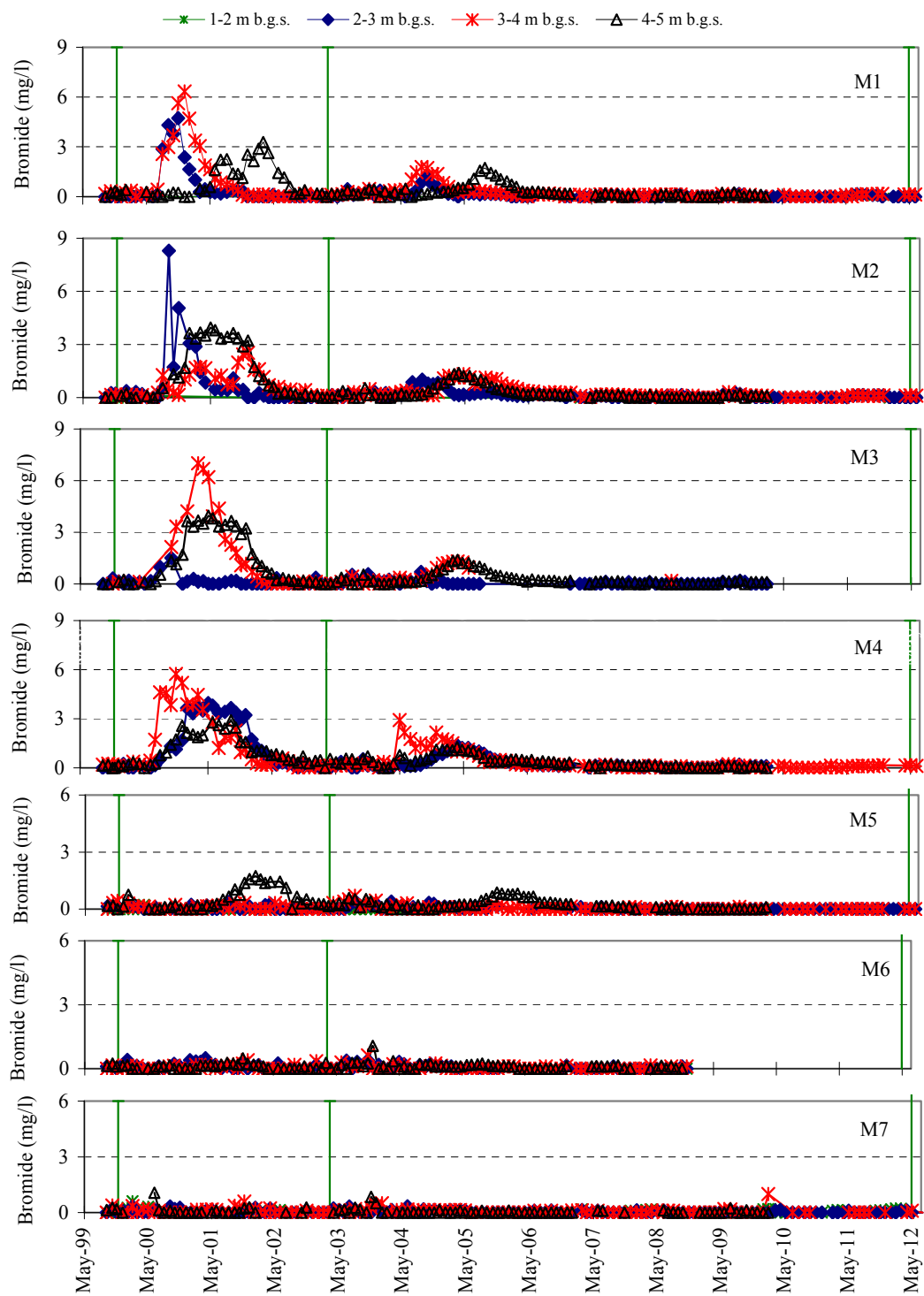
Figure 3.4. Bromide concentration in the groundwater at **Jyndevad**. The data derive from monitoring wells M1–M7. Monitoring at well M6 was suspended September 2008 (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.
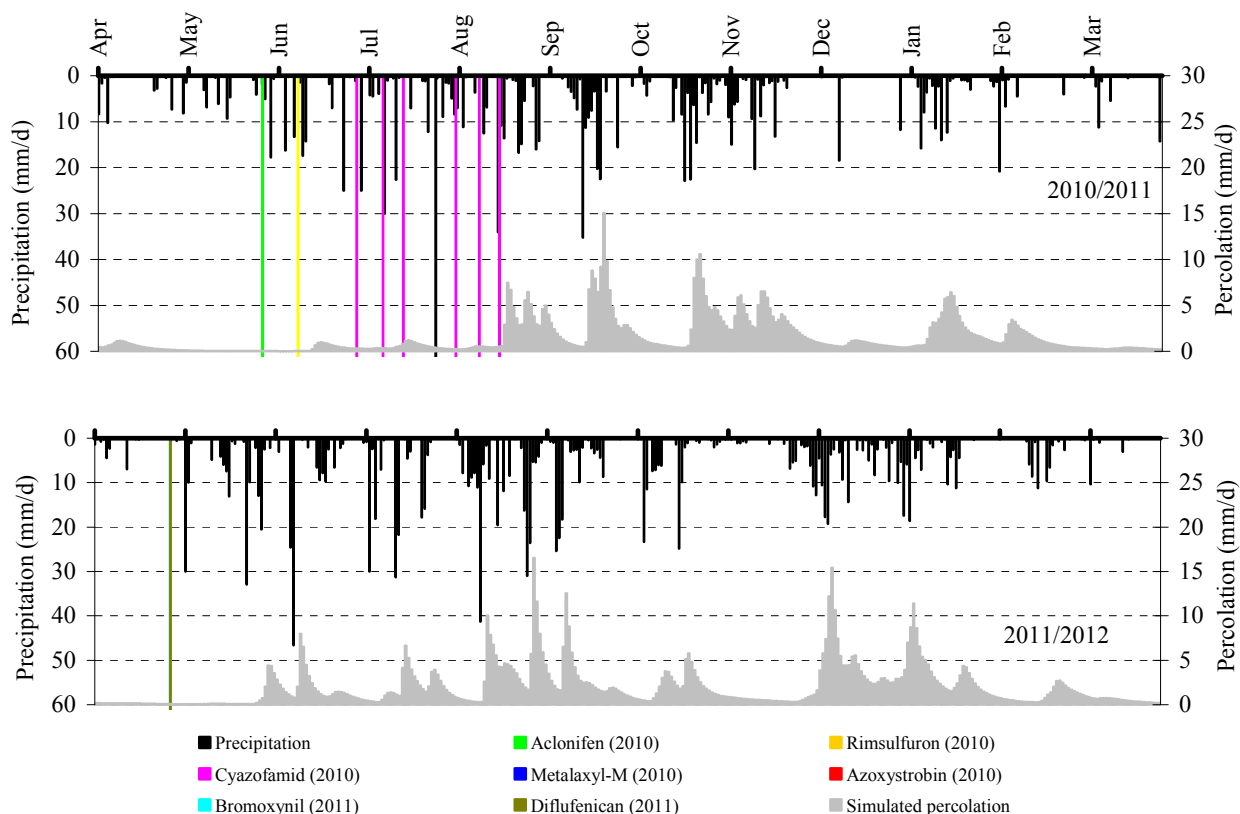
Figure 3.5. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Jyndevad** in 2010/2011 (upper) and 2011/2012 (lower).

3.2.3 Pesticide leaching

Monitoring at Jyndevad began in September 1999 and presently encompasses several pesticides and their degradation products, as indicated in Appendix 7. Pesticide application during the most recent growing seasons is listed in Table 3.2 and shown together with precipitation and simulated precipitation in Figure 3.5. It should be noted that precipitation is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model. It should also be noted that as rimsulfuron (applied here as Titus) degrade rapidly, the leaching risk is therefore associated with the degradation products: PPU and PPU-desamino, rather than the parent compounds. For the same reasons the degradation products and not the parent compounds are monitored in PLAP (Table 3.2). Pesticides applied later than April 2011 are not evaluated in this report and hence not included in Table 3.2.

The current report focuses on the pesticides applied from 2010 and onwards, while leaching risk of pesticides applied before 2010 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

Table 3.2. Pesticides analysed at **Jyndevad**. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Precip 1st year, Percol 1st year) and first month (Precip 1st month, Percol 1st year) after the first application C$_{mean}$ refers to average leachate concentration at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.2) for previous applications of pesticides. (End monito.) end of monitoring of pesticide or metabolite.

Crop	Applied product	Analysed pesticide	Applica. date	End monito.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol.	C$_{mean}$
Triticale 2007	Atlantis WG	Mesosulfuron-methyl(P)	Oct 06	Dec 09	1346	809	95	73	<0.01
		Mesosulfuron(M)	Oct 06	Dec 09	1346	809	95	73	<0.02
	Cycocel 750	Chlormequat(P)	Apr 07	Jun 08	1223	638	79	1	<0.01
	Opus	Epoxiconazole(P)	May 07	Dec 09	1193	644	123	6	<0.01
Winter Wheat 2008	Folicur EC 250	Tebuconazole(P)	Dec 07	Mar 10	1396	827	60	97	<0.01
	Pico 750 WG	Picolinafen(P)	Oct 07	Mar 10	1418	777	77	55	<0.01
	Pico 750 WG	CL153815(M)	Oct 07	Mar 10	1418	777	77	55	<0.01
Spring Barley 2009	Basagran M75	Bentazone(P)	May 09	Jun 12*	1178	630	144	13	<0.01-0.04
	Bell	Epoxiconazole(P)	May 09	Dec 09	1181	630	164	42	<0.01
	Fox 480 SC	Bifenox(P)	Apr 09	Jun 12	1206	630	106	3	<0.02
	Fox 480 SC	Bifenox acid(M)	Apr 09	Jun 12	1206	630	106	3	<0.05
	Fox 480 SC	Nitrofen(M)	Apr 09	Jun 12	1206	630	106	3	<0.01
Potatoes 2010	Fenix	Aclonifen(P)	May 10	Jun 12	1149	567	123	10	<0.01
	Ranman	Cyazofamid(P)	Jun 10	Jun 12	1188	627	125	16	<0.01
	Titus WSB	PPU(M)	Jun 10	Jun 12*	1160	592	137	13	0.02[1]
		PPU-desamino(M)	Jun 10	Jun 12*	1160	592	137	13	<0.01[1]
	Ridomil Gol MZ Pepite	Metalaxyl-M(P)	Jul 10	Jun 12*	1073	613	161	41	0.02[1]
		CGA 108906(M)	Jul 10	Jun 12*	1073	613	161	41	0.37-0.66[2]
		CGA 62826(M)	Jul 10	Jun 12*	1073	613	161	41	0.16[2]-0.19
Spring Barley 2011	DFF	Diflufenican(P)	Apr 11	Jun 12*	1315	742	126	3	<0.01
		AE-05422291(M)	Apr 11	Jun 12*	1315	742	126	3	<0.01
		AE-B107137(M)	Apr 11	Jun 12*	1315	742	126	3	<0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
[1]*C$_{mean}$ is only calculated from suction cups S1(see text).*
[2]*Degradation product of metalaxyl-M.*
monitoring continues the following year.

In Table 3.2 weighted average concentrations 1 m b.g.s. (C$_{mean}$) is calculated from both S1 and S2. When these values are reported as a range it indicated that C$_{mean}$ in S1 and S2 differs from each other. During the monitoring period 2011/2012 it was unfortunately not possible to extract sufficient water from S2 to perform all pesticide analysis. For some of the compounds (metalaxyl-M, PPU, PPU-desamino) there was not sufficient data to calculate weighted leachate concentration (Figure 3.6, 3.7 and 3.8), why reported 2010 values in Table 3.2 refers to suction cups S1 only (see note 1 in Table 3.2). For the same reason concentration of CGA62826 and CGGA 108906 in S2 was not measured in S2 during the first months after applications. In Table 3.2 calculation concentration of CGA62826 and CGA 108906 in S2 being 0.16 and 0.66 respectively refers to average leaching concentration from date of first analysis on 4 November 2010 until 1 July 2011 (see note 2 in Table 3.2). In the monitoring year 2011-2012 however samples were taken during the monitoring year and CGA 62826 and CGA 108906 were analysed in 12 samples from S1 and S2.
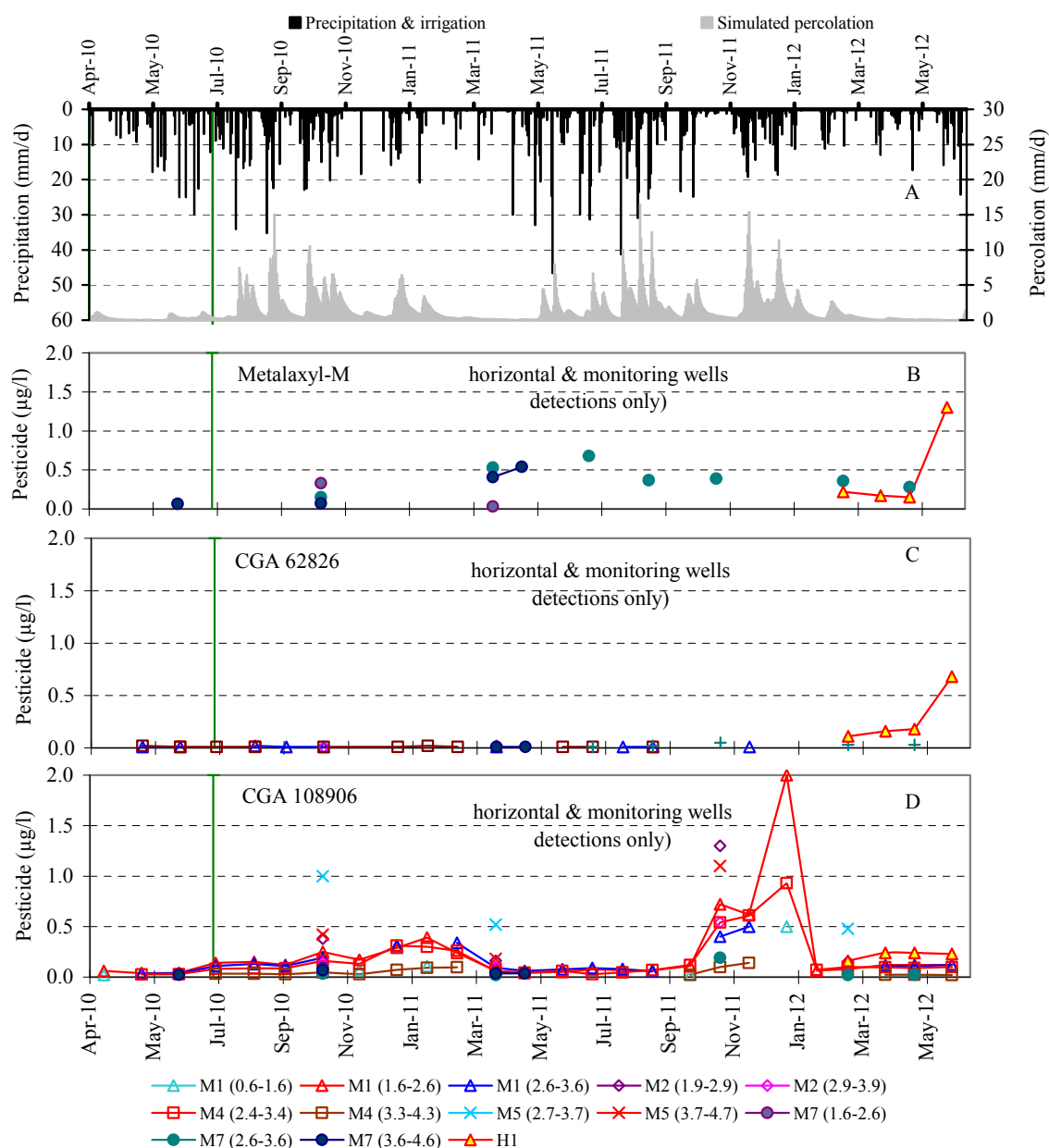
Figure 3.6. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations (µg/L) in downstream (M1, M2, M4 and H1) and upstream horizontal & monitoring wells (M7) of *metalaxyl-M* (B), CGA 62826 (C) and CGA 108906 (D) at Jyndevad. The numbers in parentheses indicate the depths of the analysed screens. The green vertical line indicates the date of pesticide application.

The degradations products, CGA 62826 and CGA 108906, average and median concentrations for S1 and S2 are shown in table 3.3. Both metabolites are in 2011/12 fund in concentrations higher than in 2010/11.

Both metalaxyl-M applied on potatoes in 2010 as well as its two degradation product for CGA 62829 and CGA 108909 leached from the root zone (1 m b.g.s.) the two latter in average concentrations exceeding 0.1 µg/L (Table 3.2, 3.3 and Figure 3.6 and 3.7). Both degradation products were found is suction cups 1 m b.g.s. in the end of the last monitoring period, indicating that leaching had not yet ceased.

Table 3.3. CGA 108906 and CGA 62826, **Jyndevad**. Average and median concentrations calculated for al watersamples with findings from S1 and S2 in the monitoring year 2011/12. CGA 108906 was found in al samples from S1 and S2 while CGA 62826 was fund in al samples from S1 and I 11 out of 12 samples from S2.

2011-2012		S1 µg/L	S2 µg/L
CGA 108906	Average	0.26	0.88
	Median	0.12	0.23
Samples with findings		12	12
CGA 62826	Average	0.12	0.08
	Median	0.08	0.07
Samples with findings		12	11
% findings		100	96
% findings >= 0.1 µg/L		54	54

Results from the saturated zone suggested that previous application occurring at up streams neighbouring fields also have induced leaching to the groundwater of metalaxyl-M, CGA 62829 and CGA108909. All three compound were present in groundwater before metalaxyl-M was applied to the field. They were also detected in samples collected from M7 situated upstream of the field site (Figure 3.6) and CGA 108909 was also found in M5 located north of the field. As the tracer test suggested that water sampled in M7 and M5 (uppermost three filters) had not infiltrated at the PLAP site, but originated from the upstream neighbouring fields where metalaxyl-M have also been applied (Brüsch et al., 2013: appendix 7). Moreover, CGA108909 was found in all groundwater samples collected 27 July 2010. As this sampling was done only 2 days after application and precipitation during this period amounted to only 0.5 mm these detections are likely to occur from previous applications as well.

The background concentration of CGA 108909 found in all monitoring wells makes it difficult to determine whether the elevated concentrations observed in downstream monitoring wells during the two year monitoring period are due to the metalaxyl-M applied on the PLAP test site in 2010 or to previous application on the "upstream" fields. However, with a background level of CGA 108909 ranging between 0.014–0.14 µg/L additional input via root zone leaching is likely to increase groundwater concentration and by this the frequency of exeedance of the 0.1 µg/L in collected groundwater samples.

In 2010/11 CGA 108906 was found in 90% of analysed groundwater samples, and 38% of analysed samples had concentration exceeding 0.1 µg/L. In 2011/12 CGA 108906 was fund in 92% of the watersamples and in 55% exceeding 0.1 µg/L, Table 3.4. The average and median concentrations were 0.24 and 0.11 µg/L.

In the new horizontal well, H1, CGA 108906, was fund in 4 analysed samples from Marts to June in concentrations from 0.16-0.24 µg/L, Figure 3.6.
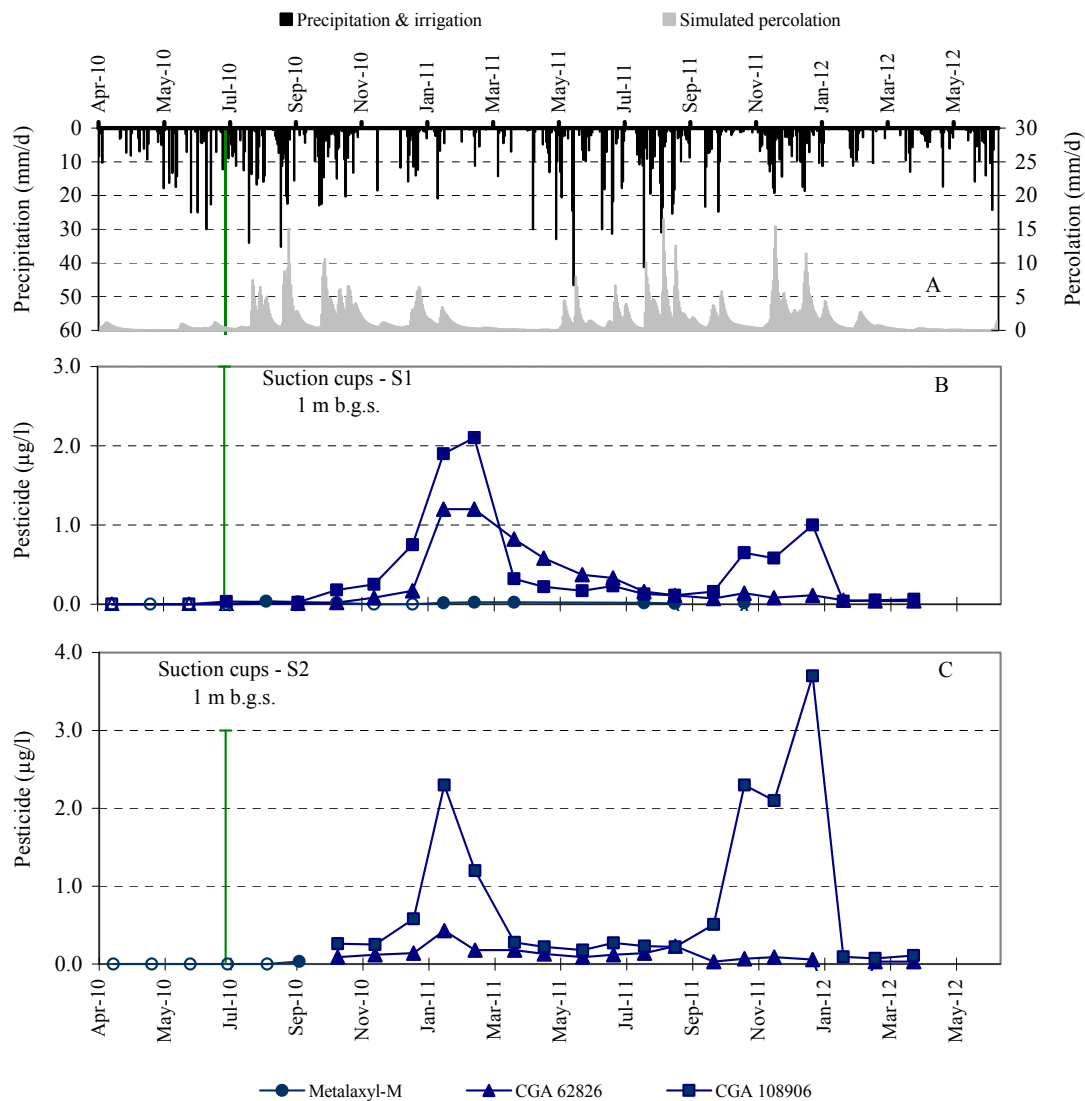
Figure 3.7. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of *Metalaxyl-M,* CGA 62826 and CGA 108906. The green vertical line indicates the date of pesticide application.

Metalaxyl-M was detected in the upstream well M7 in high concentrations reaching 0.68 µg/L, and metalaxyl-M was not fund in the downstream groundwater monitoring wells, but metalaxyl-M was found in H1 in 4 samples in concentrations reaching 1,3 µg/L in June 2012. CGA 62826 was only found in small concentrations in the vertical groundwater wells, but in H1 CGA 62826 was fund in increasing concentrations from Marts 2012 to June 2012, 0.11µg/L to 0.68 µg/L.

Table 3.4. CGA 108906 in groundwater from downstream wells, **Jyndevad**. Average and median concentrations calculated for groundwater samples with findings in 2011/12. Water samples from M7 not included.

July 2011- June 2012	
Number of groundwater samples	60
Groundwater samples with findings	55
Groundwater samples ≥ 0.1 µg/L	33
% findings (detection level- 0.02 µg/L)	92%
% findings ≥0.1 µg/L	55%
Average concentration in µg/L	0.24
Median concentration in µg/L	0.11

Metalaxyl was on the Danish market from 1980-1995, reported maximum allowed dosage from 1984-1995 being 375 gr. a.i./ha. It re-entered the Danish marked in 2007 as Metalaxyl-M with a maximum allowed dosage of 77.6 g/ha. Since 2006 metalaxyl-M was applied at upstream neighbouring fields where reported dosage did not exceed the maximum allowed dosage of 77.6 g a.i./ha but evidence of higher dosage used in the period 1988 1993 was also reported. For placing the result into regulatory context it would thus be important to judge if measured groundwater residues origin from initial high usage of 375 g a.i/ha allowed in 1980-1995 or from the current usage of 77.6 g a.i/ha allowed since 2007. Based on available data we conclude that detected residues in the groundwater derive from current usage of metalaxyl allowed since 2007 and not the initial usage allowed from 1980–1995. With an average travel time to all monitoring wells being less than 3 years (Laier et al. in prep) it is unlikely that water sampled from these screen have infiltrated the unsaturated zone before 1995, 17 years ago.

A possibility could however be that the residues originating from the initial usage of 375 g/ha (allowed in 1980-1995) were left in the soil and continued to leached during a long period of time. Should this be the case the persistency of these compounds would be very high allowing them to leach more than a decade after application. An assumption which does not correspond with the regulatory assessment, where the final endpoints for DT_{50} were less than 18 days (Danish EPA, 2007).

The herbicides bifenox and bentazone and the fungicide epoxiconazole were used in the spring barley sown in 2009.

Bifenox was found twice in suctions cups, in concentrations of 0.034 and 0.036 µg/L, four to six months after the application as well as in two monitoring wells five months after application, in concentrations of 0.05 and 0.033 µg/L (Appendix 5, Table A5.2). The metabolite bifenox acid was found once, 0.1 µg/L, in a monitoring well four months after application, while nitrofen was not detected in any analysed water sample. In 2011/12 neither of the 3 substances were found in groundwater or in the unsaturated zone.

Bentazone was absent in all the samples from the monitoring wells. It was, however, found frequently in samples from suction cups, reaching a maximum of 0.71 µg/L, (see Figure 15 in Kjær et al 2011). None of the substances were leached in yearly average concentrations exceeding 0.1 µg/L (Table 3.2).

Epoxiconazole did not leach at Jyndevad, as it was never detected in any of the analysed water samples.

Aclonifen and cyazofamid both applied on potatoes in 2010 did not leach during the monitoring period from 2010 to June 2012, as none of the compounds was found in any of the analysed water samples (Appendix 5).

Diflufenican was used in spring barley in 2011. Diflufenican and the two degradation products, AE-05422291 and AE-B107137, did not leach from the root zone and neither was found in water samples from the unsaturated zone or in the groundwater from April 2011 to June 2012.

Rimsulfuron (Titus WSB) was applied on potatoes in 2010 in the same dosage as that used on potatoes in 2002. Rimsulfuron degrades rapidly in the soil, and the leaching risk is therefore associated with the degradation products PPU and PPU-desamino. Following the 2002 application both compounds were characterised by continuous leaching over a long period of time. Average yearly concentrations of especially PPU reaching 0.1 µg/L were seen as long as three years after 2002 application (Rosenbom et al., 2010a). Although the concentration decreased during the 2009/2010, PPU could occasionally still be found in low concentrations. Additional leaching was observed after the 2010 application. In 2011/12 there was found concentration of PPU reaching 0.18 µg/L in H1, 0.1 µg/L in M4 and in suction cups S1 and S2 0.19 and 0.1 µg/L.

In 2011/12 PPU was found frequently but in small concentrations in the deeper screens of M4, and in rather high concentrations in H1. Also PPU-desamino was found in M4 and in H1.

The results of the 2002 application are summarized in Rosenbom et al. (2010a).

4 Pesticide leaching at Silstrup

4.1 Materials and methods

4.1.1 Site description and monitoring design

The test field at Silstrup is located south of Thisted in north-western Jutland (Figure 1.1). The cultivated area is 1.7 ha (91 x 185 m) and slopes gently 1–2° to the north (Figure 4.1). Based on two profiles excavated in the buffer zone bordering the field the soil was classified as Alfic Argiudoll and Typic Hapludoll (Soil Survey Staff, 1999). The topsoil content of clay in the two profiles was 18% and 26%, and the organic carbon content was 3.4% and 2.8%, respectively (Table 1.1). The geological description showed rather homogeneous clay till rich in chalk and chert, containing 20–35% clay, 20–40% silt and 20–40% sand. In some intervals the till was sandier, containing only 12–14% clay. Moreover, thin lenses of silt and sand were found in some of the wells. The gravel content was approx. 5%, but could be as high as 20%. A brief description of the sampling procedure is provided in Appendix 2 and the analysis methods in Kjær et al. (2002). The monitoring design and test site are described in detail in Lindhardt et al. (2001). In September 2011, the monitoring system was extended with three horizontal screens (H3) 2 m b.g.s. in the North-Eastern corner of the field (Figure 4.1) - one of the screens should be located just below the drain 1.1 m b.g.s. A brief description of the drilling and design of H3 is given in Appendix 8.

4.1.2 Agricultural management

Management practice during the 2011-2012 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.3). For information about management practice during the previous monitoring periods, see previous reports available on http://pesticidvarsling.dk/publ_result/index.html.

The crop of the field was a 2nd year crop of red fescue (cv. Jasperina) that had been under sown in spring barley 11 April 2009. On 15 April 2011 the red fescue was sprayed with the fungicide iodosulfuron-methyl-sodium. However, the substance was not included in the monitoring programme. On the 26 April the herbicide fluazifop-P-butyl was used. On 21 July the grass seed yielded 15.2 hkg/ha of seeds (87% dry matter), nearly twice the average for the soil type this year (Plantedirektoratet, 2011), and 45.8 hkg/ha of straw (100% dry matter) being baled and removed from the field on 30 July.
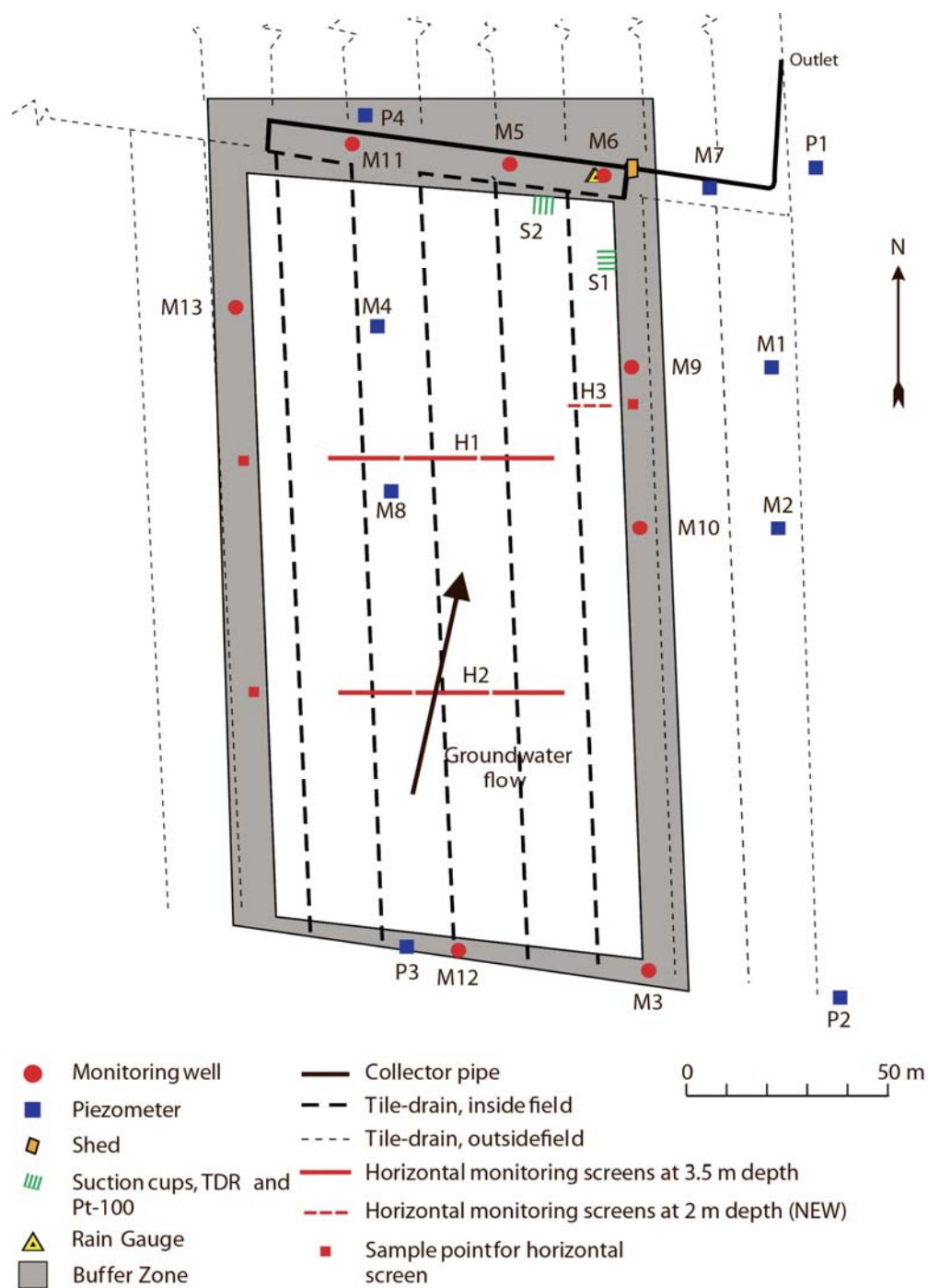
Figure 4.1. Overview of the **Silstrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted weekly from the drainage system (during period of continuous drainage runoff) and monthly and half-yearly from selected vertical and horizontal monitoring screens as described in Table A2.1 in Appendix 2.

4.1.3 Model setup and calibration

Compared with the setup in Brüsch *et al.* (2013), a year of validation was added to the MACRO setup for the Silstrup site. The setup was hereby calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2012. For this purpose, the following time series have been used: the observed groundwater table measured in the piezometers located in the buffer zone, soil water content measured at three depths (25, 60, and 110 cm b.g.s.) from the two profiles S1 and S2 (Figure 4.1), and the measured drainage flow. Data acquisition, model setup and results related to simulated bromide transport are described in Barlebo *et al.* (2007). Given impounding of water in the drainage water monitoring well, estimates for the measured drainage on 11 December 2006, 13-14 December 2006, 28 February 2007, 23 October 2011, 13 November 2011 and 11 December 2011 were based on expert judgement. Additionally, TDR-measurements at 25 cm b.g.s. in the period 15 December 2009–20 March 2010 were discarded given freezing soils (soil temperatures at or below zero degrees Celsius). The soil water content is measured with TDR based on Topp calibration (Topp *et al.*, 1980), which will underestimate the total soil water content at the soil water freezing point as the permittivity of frozen water is much less than that of liquid water (Flerchinger *et al.*, 2006).

4.2 Results and discussion

4.2.1 Soil water dynamics and water balances

The model simulations were consistent with the observed data, thus indicating a reasonable model description of the overall soil water dynamics in the unsaturated zone (Figure 4.2). As in Brüsch *et al.* (2013), the simulated groundwater table of this hydraulic year was validated against the much more fluctuating groundwater table measured in piezometer P3, which yielded the best description of measured drainage (Figure 4.2B and 4.2C). The drainage flow period of the past year was well captured by the model (Figure 4.2C). As in the previous monitoring periods, the overall trends in soil water content were described reasonably well (Figure 4.2D, 4.2E, and 4.2F), although the model describe the topsoil as being more wet during the summer period than measured by the upper TDR probes (Figure 4.2D).
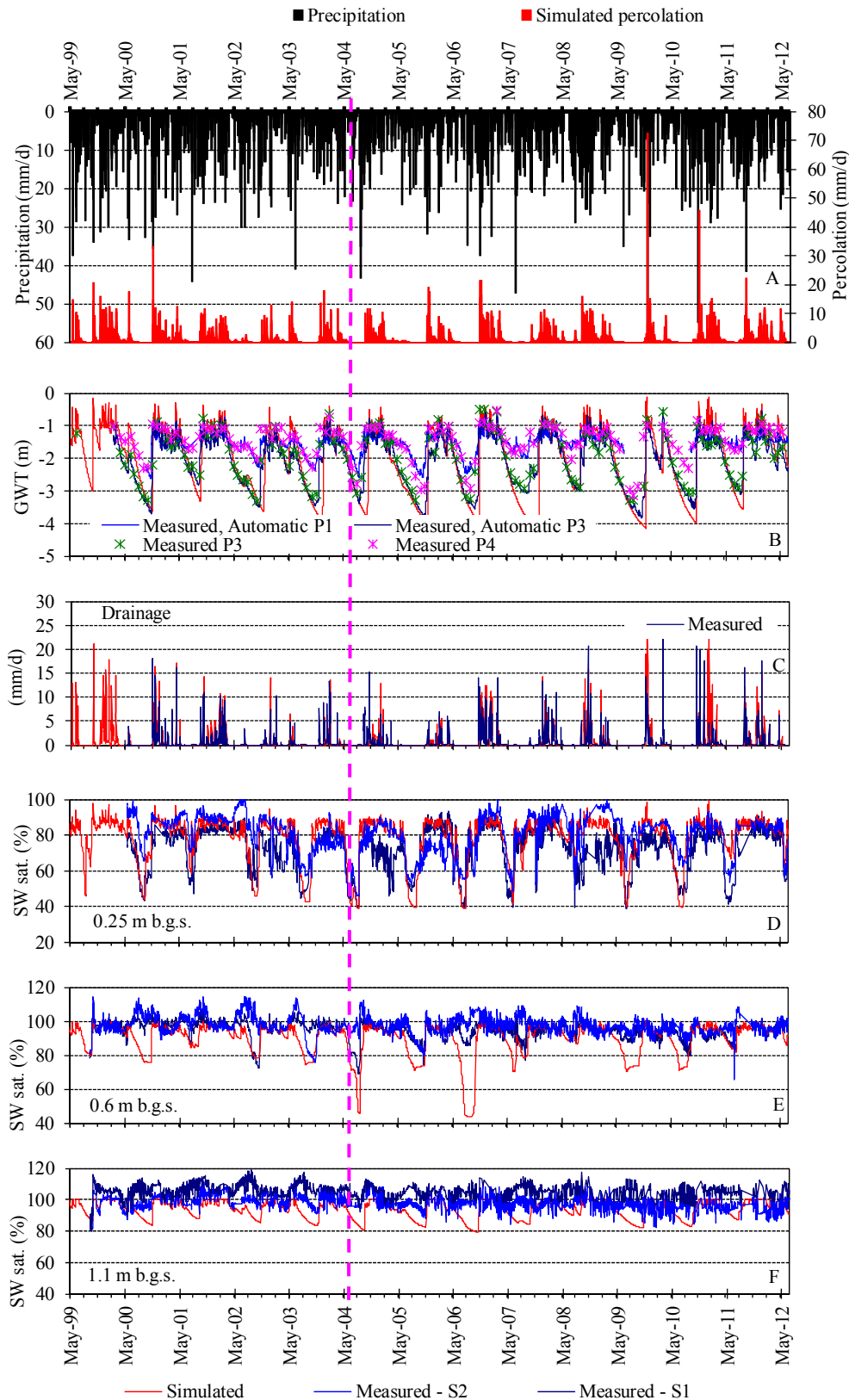
Figure 4.2. Soil water dynamics at **Silstrup**: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E, and F). The measured data in B derive from piezometers located in the buffer zone. The measured data in D, E, and F derive from TDR probes installed at S1 and S2 (Figure 4.1). The broken vertical line indicates the beginning of the validation period (July 2004-June 2012).

Table 4.1. Annual water balance for **Silstrup** (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation[2]	Precipitation	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge[3]
1.7.99–30.6.00[1]	976	1175	457	–	443	275[4]
1.7.00–30.6.01	976	909	413	217	232	279
1.7.01–30.6.02	976	1034	470	227	279	338
1.7.02–30.6.03	976	879	537	81	74	261
1.7.03–30.6.04	976	760	517	148	97	94
1.7.04–30.6.05	976	913	491	155	158	267
1.7.05–30.6.06	976	808	506	101	95	201
1.7.06–30.6.07	976	1150	539	361	307	249
1.7.07–30.6.08	976	877	434	200	184	242
1.7.08–30.6.09	976	985	527	161	260	296
1.7.09–30.6.10	976	835	402	203	225	230
1.7.10–30.6.11	976	1063	399	172	569	492
1.7.11–30.6.12	976	1103	429	230	321	444

[1] The monitoring started in April 2000.

[2] Normal values based on time series for 1961–1990 corrected to soil surface.

[3] Groundwater recharge calculated as precipitation - actual evapotranspiration - measured drainage.

[4] Where drainage flow measurements were lacking, simulated drainage flow was used to calculate groundwater recharge.

The resulting water balance for Silstrup for the entire monitoring period is shown in Table 4.1. Compared with the previous 12 years, the recent hydraulic year July 2010-June 2012 was characterised by having the third highest precipitation, the fourth lowest simulated actual evapotranspiration, and the second highest measured drainage. Precipitation of this year was characterised by a very wet July-September, dry October-November, wet December-January, and February-Marts being very dry (Appendix 4). Due to this precipitation pattern, the simulated percolation pattern of the year July 2011-June 2012, continuous percolation was simulated for the hole hydrological year except for a few days in June and July (Figure 4.2A). The climatic setting of this year gave rise to a long period with the groundwater table just fluctuating at the drainage level, causing a very high measured drainage compared to the other hydrological years included in PLAP (Figure 4.2B and 4.2C).
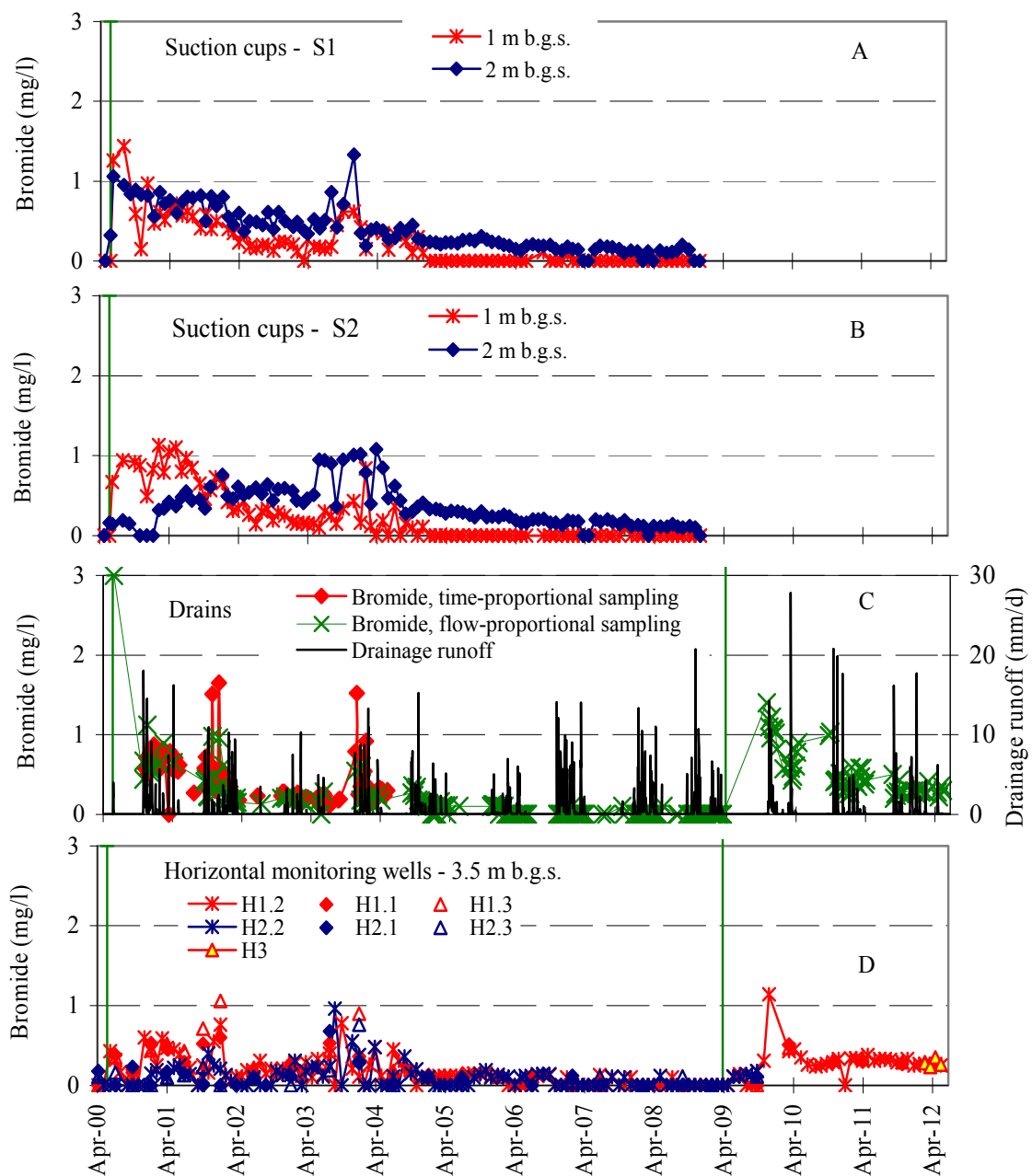
Figure 4.3. Bromide concentration at **Silstrup**. A and B refer to suction cups located at S1 and S2 (see Figure 16). The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells H1, H2 and H3 (D). In March 2009, bromide measurements in the suction cups were suspended (Appendix 2). The green vertical lines indicate the dates of bromide applications.

4.2.2 Bromide leaching

The bromide concentrations shown in Figure 4.3 and Figure 4.4 relate to the bromide applied in May 2000, as described in previous reports (Kjær *et al.* 2003 and Kjær *et al.* 2004) and further evaluated in Barlebo *et al.* (2007). In Marts 2009, bromide measurements in the suction cups and monitoring wells M6 and M11 were suspended. In April 2009, 31.5 kg/ha potassium bromide was applied for the second time.
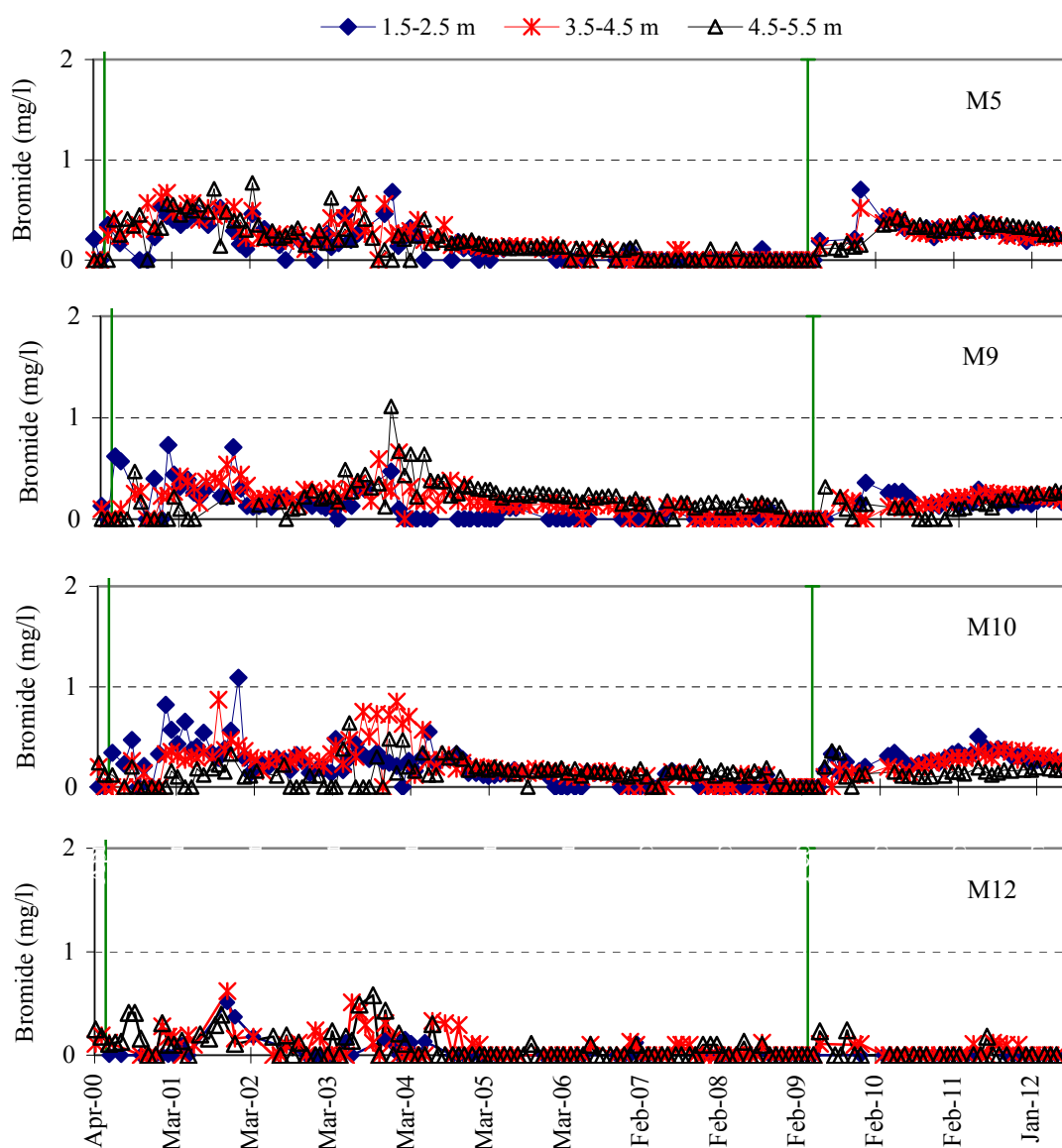
Figure 4.4. Bromide concentration at **Silstrup**. The data derive from the vertical monitoring wells (M5–M12). In September 2008, monitoring wells M6 and M11 were suspended (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the date of bromide applications.

4.2.3 Pesticide leaching

Monitoring at Silstrup began in May 2000 and several pesticides and their degradation products have been monitored, Appendix 7. Pesticide application during the most recent growing seasons, 2010/2011 and 2011/2012 is listed in Table 4.2 and shown together with precipitation and simulated percolation in Figure 4.5. It should be noted that precipitation in Table 4.2 is corrected to soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model. Moreover, pesticides applied later than April 2012 are not evaluated in this report and hence not included in Table 4.2.

Table 4.2. Pesticides analysed at **Silstrup**. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Precip 1st year, Percol 1st year) and first month (Precip 1st month, Percol 1st year) after the first application. C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8, Table A8.3 for previous applications of pesticides. (End monito.) end of monitoring of pesticide or metabolite.

Crop	Applied product	Analysed pesticide	Applica. date	End Monito.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol.	C_{mean}
Winter Wheat 2007	Cycocel 750	Chlormequat(P)	Apr 07	Jun 08	966	382	30	3	<0.01
	Hussar OD	Iodosulfuron-methyl(P)	Apr 07	Oct 10	966	382	30	3	<0.01
		Metsulfuron-methyl(P)	Apr 07	Oct 10	966	382	30	3	<0.01
	Opus	Epoxiconazole(P)	Jun 07	Apr 09	947	407	173	0	<0.01
	Stomp Pentagon	Pendimethalin(P)	Sep 06	Apr 08	1166	508	111	0	0.04
Fodder Beet 2008	Fusilade Max	Fluazifop-P(M)	Jul 08	Jun 12*	985	494	105	21	<0.01
		TFMP(M)	Jul 08	Jun 12*	985	494	105	21	0.24
	Goliath	Metamitron(P)	May 08	Dec 10	969	498	43	4	0.01
		Desamino-metamitron(M)	May 08	Dec 10	969	498	43	4	0.02
	Safari	Triflusulfuron-methyl(P)	May 08	Jun 10	969	498	43	4	<0.01
		IN-D8526(M)	May 08	Jun 10	969	498	43	4	<0.01
		IN-E7710(M)	May 08	Jun 10	969	498	43	4	<0.01
		IN-M7222(M)	May 08	Jun 10	969	498	43	4	<0.02
	Tramat 500 SC	Ethofumesate(P)	May 08	Dec 10	979	497	68	3	<0.01
Spring Barley 2009	Amistar	Azoxystrobin(P)	Jun 09	Mar 12	835	390	61	0	0.01
		CyPM(M)	Jun 09	Mar 12	835	390	61	0	0.06
	Fighter 480	Bentazone(P)	May 09	Jun 11	876	391	85	1	0.03
Red Fescue 2010	Fox 480 SC	Bifenox(P)	Sep 09	Jun 12*	888	390	56	0	<0.02
		Bifenox acid(M)	Sep 09	Jun 12*	888	390	56	0	2.26
		Nitrofen(M)	Sep 09	Jun 12*	888	390	56	0	<0.01
	Fusilade Max	Fluazifop-P(M)	May 10	Jun 12*	1027	520	53	2	<0.01
		TFMP(M)	May 10	Jun 12*	1027	520	53	2	<0.02
	Hussar OD	Iodosulfuron-methyl(P)	Aug 09	Dec 10	898	390	27	0	<0.01
		Metsulfuron-methyl(M)	Aug 09	Dec 10	898	390	27	0	<0.01
		Triazinamin(M)	Aug 09	Dec 10	898	390	27	0	<0.01
	Hussar OD	Iodosulfuron-methyl(P)	May 10	Dec 10	1024	520	49	1	<0.01
		Metsulfuron-methyl(M)	May 10	Dec 10	1024	520	49	1	<0.01
Red Fescue 2011 Season 2	Fusilade Max	TFMP(M)	May 11	Jun 12*	1043	550	26	4	0.003
Red Fescue 2011/12 Season 3	Fox 480 SC	Bifenox(P)	Sep 11	Jun 12*	774	476	101	68	0.01
	Fox 480 SC	Bifenox acid(M)	Sep 11	Jun 12*	774	476	101	68	0.47
	Fox 480 SC	Nitrofen(M)	Sep 11	Jun 12*	774	476	101	68	0.01
	Fusilade Max	TFMP(M)	Apr 12	Jun 12*	222	72	127	64	0.19
	DFF	*Diflufenican(P)*	*May 12[1]*	*Jun 12**	*227*	*76*	*112*	*56*	*0.08*
	DFF	*AE-05422291(M)*	*May 12[1]*	*Jun 12**	*227*	*76*	*112*	*56*	*0.00*
	DFF	*AE-B107137(M)*	*May 12[1]*	*Jun 12**	*227*	*76*	*112*	*56*	*0.12*

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
[1])*Applied after April 2012.*
monitoring continues the following year.
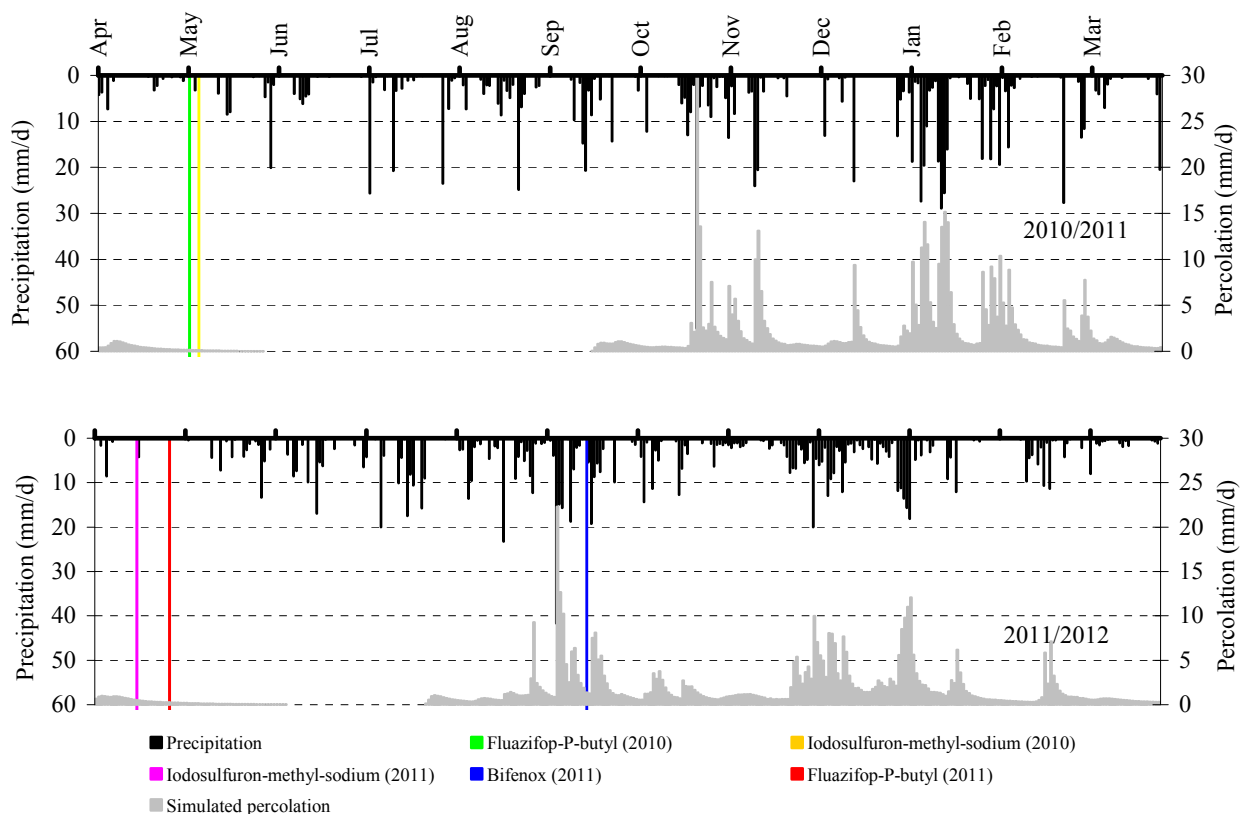
Figure 4.5. Pesticides included in the monitoring programme, precipitation and irrigation (primary axis) and simulated percolation 1 m b.g.s. (secondary axis) at **Silstrup** in 2010/2011 (upper) and 2011/2012 (lower).

It should also be noted that as fluazifop-P-butyl (Fusilade Max) degrade rapidly, the leaching risk is associated with the degradation products fluazifop-P and TFMP rather than the parent products. For the same reasons the degradation products and not the parent compounds have been monitored in the PLAP (Table 4.2).

The current report focuses on the pesticides applied from 2010 and onwards, while the leaching risk of pesticides applied in 2009 and before has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

The herbicide fluazifop-P-butyl has been included in the PLAP at Silstrup four times, and as fluazifop-P-butyl is rapidly degraded, focus previously has been on its degradation products firstly fluazifop-P (free acid) and lately TFMP. The metabolite fluazifop-P (free acid) was only detected once in groundwater. Since the 2008 application in fodder beet (Table 4.2) focus has been on the degradation product TFMP. In Figure 4.6 A,B and C it can be seen that an application of 375 g/ha of fluazifop-P-butyl (3.0 l/ha Fusilade Max) lead to TFMP concentrations above 0.1 µg/L in both drainage and groundwater. Further, 0.1 µg/L was exceeded first in the groundwater and then later in the drainage water, indicating a preferential transport. Subsequently, the Danish EPA has restricted the use of fluazifop-P-butyl regarding applicable amounts, crop types and frequency of applications.

When, on 2 May 2011, the fluazifop-P-butyl was applied in the red fescue, dosage had been halved to 1.5 L/ha of Fusilade Max (187.5 g/ha of fluazifop-P-butyl). This time the crop was a dense red fescue grass compared with the more open stand of fodder beet of July 2008. As can be seen from Figure 4.6 A there was no immanent leaching of TFMP to neither drains nor groundwater following the application in red fescue. One notes that there during the summer of 2009, was no drainage flow (Figure 4.6 A). It took nearly five months before 0.06 µg/L of TMP was detected in the drainage water and additional 11 months before the next detection of TFMP in the drainage water, still concentrations were less than 0.1 µg/L.

On the 19 April 2012 the red fescue was sprayed once more with 187.5 g/ha of fluazifop-P-butyl (Fusilade Max). Although the amount applied to the red fescue was identical to that of 26 April 2011, it caused a TFMP concentration in the drainage water of 0.11 µg/L, and detections as well in the new horizontal well located 2.0 m b.g.s. as well as in the two upper screens of the monitoring well M.5 located from 1.5-3.5 m b.g.s. When sampling one week later, drainage water concentrations had risen to 0.23 µg/L and on the 23 May 2012 all water sampled exceeded the threshold of 0.10 µg/L, being 0.64 µg/L in drainage, 0.13 µg/L in the horizontal well 2.0 m b.g.s., 0.11 in the horizontal well 3.5 m b.g.s. as well as 0.20 and 0.22 µg/L in the upper 2 screens of M 5 (Figure 4.6).

In total fluazifop-P-butyl has now been applied four times at the Silstrup site. In the first of two instances the crop was fodder beet. The monitoring of the first application focused solely on the metabolite fluazifop-P (free acid), being detected only once in a concentration of 0.072 µg/L (data not shown, see Kjær et al., 2003). However, when including TFMP matters changed as is seen from Figure 4.6B. TFMP was found leaching in high concentrations not only to the drainage water but also reached the groundwater, even before it had been detected in the drainage water, indicating a preferential flow pathway.

When fluazifop-P-butyl was used for the third time, April 2010, the Danish EPA had restricted its use regarding applicable amounts, crop types and frequency of applications. As seen from Figure 4.6B this seemed to have alleviated its environmental impact. However, as is also seen from 4.6B, there still seems to be problems even in the lower dosage and in the dense grass crop. Regarding the fourth applications results are preliminary, and must await a full monitoring period of two years following the application of April 2012. However, it is worth noting the difference in percolation following shortly after the spraying in 2010 and 2012.

Since the most recent application of the herbicide bifenox in the red fescue done 16 September 2011, there have been numerous detections of bifenox acid in both drainage water and groundwater. The highest concentration in drainage water being 4.8 µg/L of bifenox acid sampled on 29 September 2011 and 1.2 µg/L of bifenox acid in groundwater sampled November 2011 from the uppermost screen of monitoring well M5 (data not shown). Bifenox itself has only been found a few times in the drainage water between 22 September and 19 October 2011, concentrations ranging from 0.023 to 0.38 µg/L. Nitrofen, another degradation product of bifenox, was solely found in drainage water within the same period, concentrations ranging between 0.045 and 0.34 µg/L. Due to previous monitoring within the PLAP, the Danish EPA has now prohibited all use of bifenox.
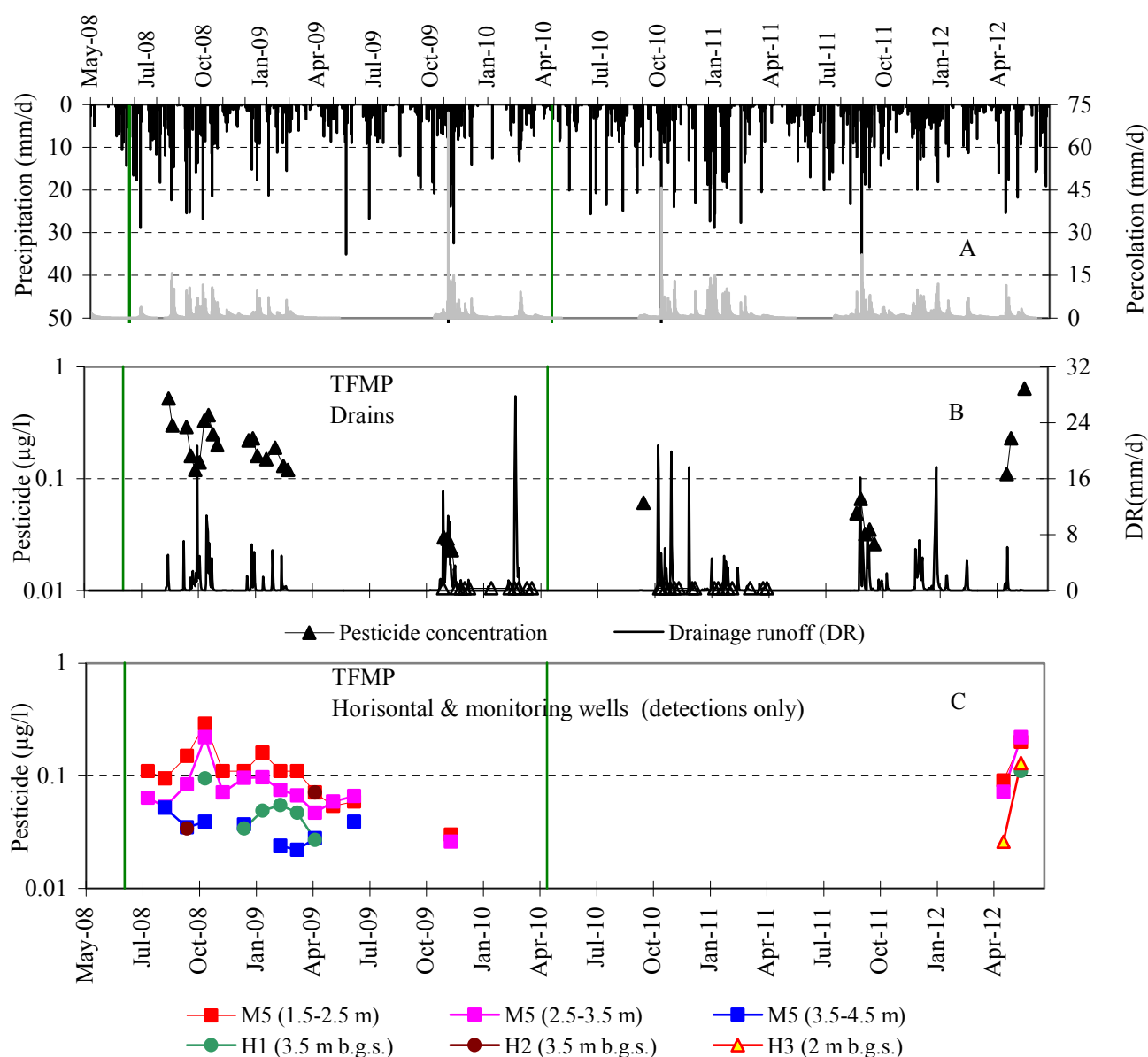
Figure 4.6. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of TFMP (B) in the drainage runoff, and the concentration of TFMP (C) in the groundwater horizontal & monitoring screens at **Silstrup**. The green vertical lines indicate the dates of fluazifop-P-butyl applications. Values below the detection limit of 0.01 µg/L are shown as 0.01 µg/L (all graphs) and further represented by open symbols in A, B and C.

Azoxystrobin has been applied at Silstrup 3 times since 2004 (Figure 4.7). Whereas the last application, done 24 June 2009, still causes leaching of the metabolite CyPM to the drainage system (Figure 4.7 C), leaching of azoxystrobin itself seems to have ended, the most recent detection being 0.011 µg/L on 24 March 2010 (Figure 4.7 B). The concentrations of the metabolite CyPM were generally higher than those of the parent compound. Whereas there have been no detections of azoxystrobin in the groundwater, CyPM was found in both horizontal and vertical wells, concentrations ranging between 0.013 and 0.086 µg/L and 0.011 and 0.1 µg/L, respectively. Latest detection of CyPM in groundwater was 0.012 µg/L on 19 May 2010 (Figure 4.7 D).
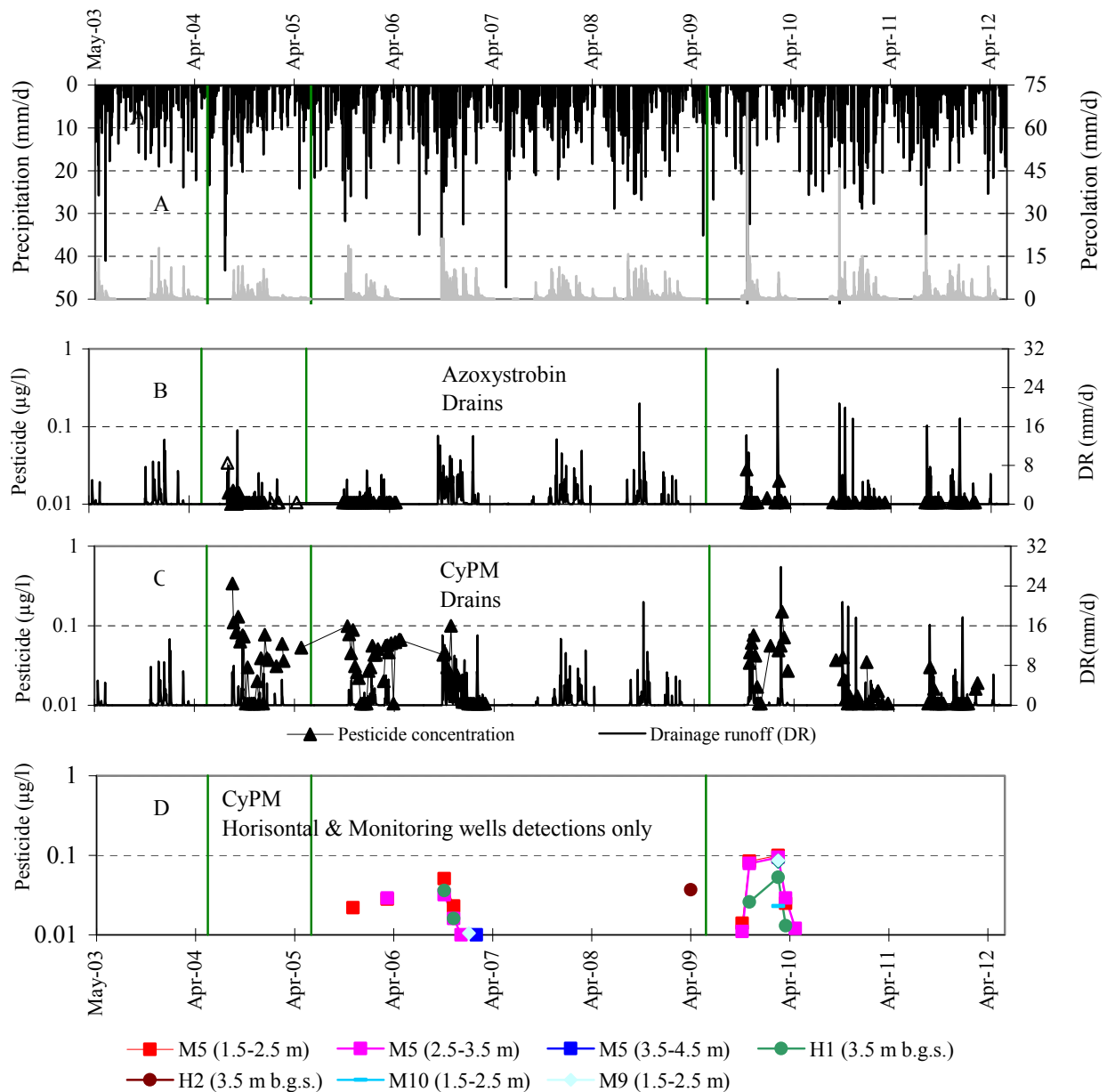
Figure 4.7. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff, and the concentration of CyPM (D) in the groundwater monitoring screens at **Silstrup**. The green vertical lines indicate the dates of bentazone and azoxystrobin applications. Values below the detection limit of 0.01 µg/L are shown as 0.01 µg/L (all graphs) and further represented as open symbols in B.

5 Pesticide leaching at Estrup

5.1 Materials and methods

5.1.1 Site description and monitoring design

Estrup is located in central Jutland (Figure 1.1) west of the Main Stationary Line on a hill-island, i.e. a glacial till preserved from the Weichselian Glaciation. Estrup has thus been exposed to weathering, erosion, leaching and other geomorphological processes for a much longer period than the other sites. The test field covers a cultivated area of 1.3 ha (105 x 120 m) and is virtually flat (Figure 5.1). The site is highly heterogeneous with considerable variation in both topsoil and aquifer characteristics (Lindhardt *et al.*, 2001). Such heterogeneity is quite common for this geological formation, however. Based on three profiles excavated in the buffer zone bordering the field the soil was classified as Abrupt Argiudoll, Aqua Argiudoll and Fragiaquic Glossudalf (Soil Survey Staff, 1999). The topsoil is characterised as sandy loam with a clay content of 10–20%, and an organic carbon content of 1.7–7.3%. A C-horizon of low permeability also characterises the site. The saturated hydraulic conductivity in the C-horizon is 10^{-8} m/s, which is about two orders of magnitude lower than at the other loamy sites (Table 1.1). The geological structure is complex comprising a clay till core with deposits of different age and composition (Lindhardt *et al.*, 2001). A brief description of the sampling procedure is provided in Appendix 2 and the analysis methods in Kjær et al. (2002). The monitoring design and test site are described in detail in Lindhardt et al. (2001). Please note that the geological conditions only allowed one of the planned horizontal wells in 3.5 m b.g.s. to be installed. In September 2011, the monitoring system was extended with three horizontal screens (H2) 2 m b.g.s. in the North-Eastern area of the field, Figure 5.1 - one of the screens should be located just below the drain 1.1 m b.g.s. A brief description of the drilling and design of H2 is given in Appendix 8.

5.1.2 Agricultural management

Management practice during the 2011-12 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.4). For information about management practice during the previous monitoring periods, see previous monitoring reports available on http://pesticidvarsling.dk/publ_result/index.html.

On the 14 September 2011 the field was ploughed and sown with winter wheat (cv. Frument). The wheat emerged on 25 September and on the 30 September, when the first leaf was through the coleoptile, the herbicide tribenuron-methyl was sprayed. At the end of tillering, 26 April 2012, the herbicide bifenox was applied. The fungicide, metrafenone was used twice on 9 May, first node above tillering node, and 7 June, when 80% of inflorescence had emerged. The winter wheat was harvested on 22 August yielding 66.3 hkg/ha of grain (85% dry matter), which was only 3/4 of the average for the soil type this year (Plantedirektoratet, 2011), whereas 53.8 hgk/ha of straw (100% dry matter) was shredded at the day of the harvest. Weeds was sprayed with the herbicide glyphosate on 3 October. Ploughing of the field was subsequently done on 9 November. Following a rotary cultivation on 29 March 2012 the field was sown with spring barley (cv. Keops) on 30 March.
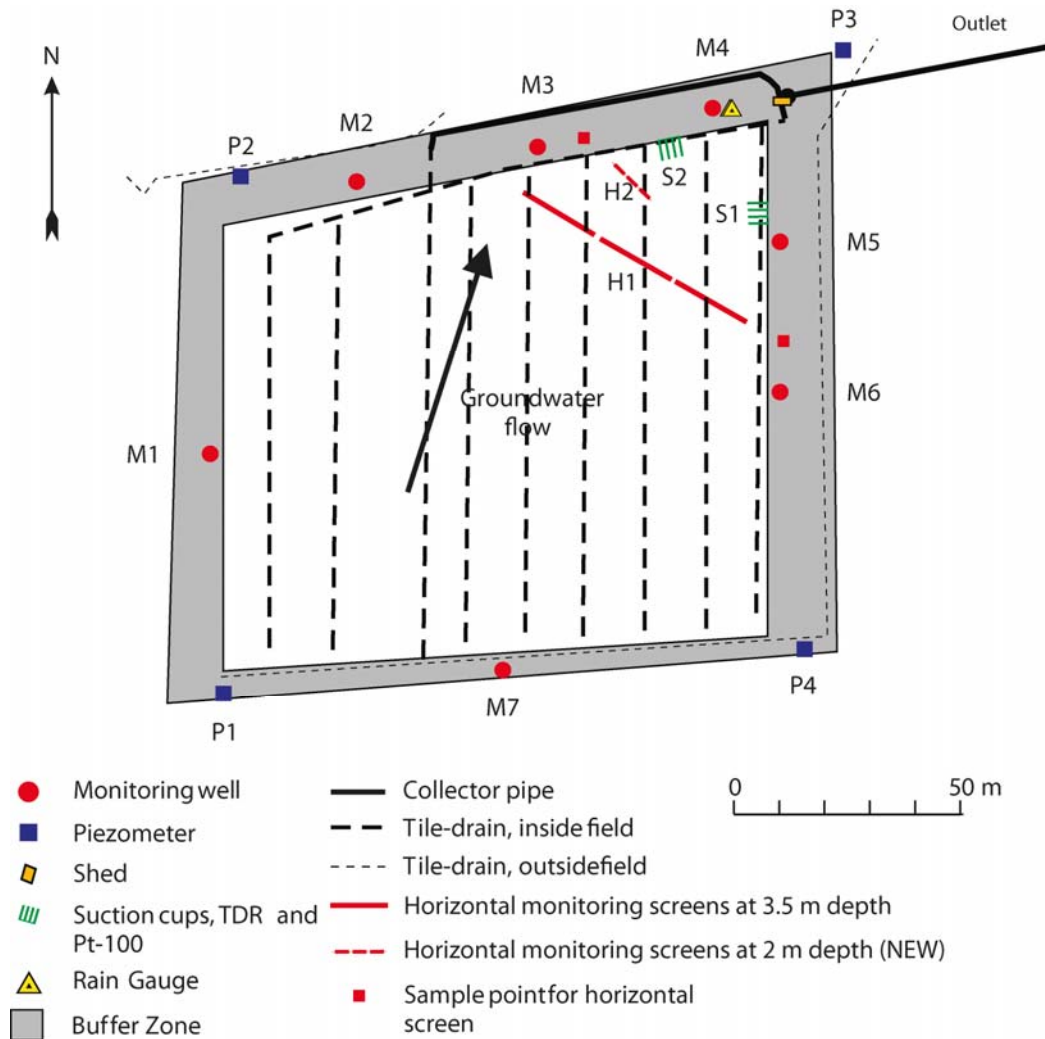
Figure 5.1. Overview of the **Estrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted weekly from the drainage system (during period of continuous drainage runoff) and monthly and half-yearly from selected vertical and horizontal monitoring screens as described in Table A2.1 in Appendix 2.

5.1.3   Model setup and calibration

The numerical model MACRO (version 5.1, Larsbo *et al.,* 2005) was applied to the Estrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the monitoring period from July 2000-June 2012 and to establish an annual water balance.

Compared to the setup in Brüsch *et al.* (2013), a year of validation was added to the MACRO setup for the Estrup site. The setup was subsequently calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2012. For this purpose, the following time series have been used: the observed groundwater table measured in the piezometers located in the buffer zone, measured drainage flow, and soil water content measured at two depths (25 and 40 cm b.g.s.) from the soil profile S1 (Figure 5.1). The TDR probes installed at the other

depths yielded unreliable data with saturations far exceeding 100% and unreliable soil water dynamics with increasing soil water content during the drier summer periods (data not shown). No explanation can presently be given for the unreliable data, and they have been excluded from the analysis. The data from the soil profile S2 have also been excluded due to a problem with water ponding above the TDR probes installed at S2, as mentioned in Kjær *et al.* (2003). Finally, TDR-measurements at 25 cm b.g.s. in February 2010 were discarded given freezing soils (soil temperatures at or below zero degrees Celsius). The soil water content is measured with TDR based on Topp calibration (Topp *et al.*, 1980), which will underestimate the total soil water content at the soil water freezing point as the permittivity of frozen water is much less than that of liquid water (Flerchinger *et al.*, 2006).

Because of the erratic TDR data, calibration data are limited at this site. Data acquisition, model setup as well as results related to simulated bromide transport are described in Barlebo *et al.* (2007).

5.2   Results and discussion

5.2.1   Soil water dynamics and water balances

The model simulations were generally consistent with the observed data (which were limited compared to other PLAP sites, as noted above), indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 5.2). The model provided an acceptable simulation of the overall level of the groundwater table. As in the previous hydrological year, a drop in the measured groundwater table was seen after short periods of low precipitation (Figure 5.2B). Also here the simulated groundwater table did not seem as sensitive to these short periods of low precipitation and tended not to drop as much as the measured values. Since the subsoil TDR data are limited, a more detailed study of soil water dynamics in these layers is difficult. However, the overall soil water saturation at 25 and 40 cm b.g.s. was captured (Figure 5.2D and 5.2E), except for the drop in water saturation at 25 cm b.g.s. in April-June 2012. Nothing special is noted for the groundwater table in the latest monitoring period (July 2010-June 2012). As in previous years (Brüsch *et al.*, 2013), the simulated groundwater table often fluctuates slightly above the drain depth during periods of drainage flow.
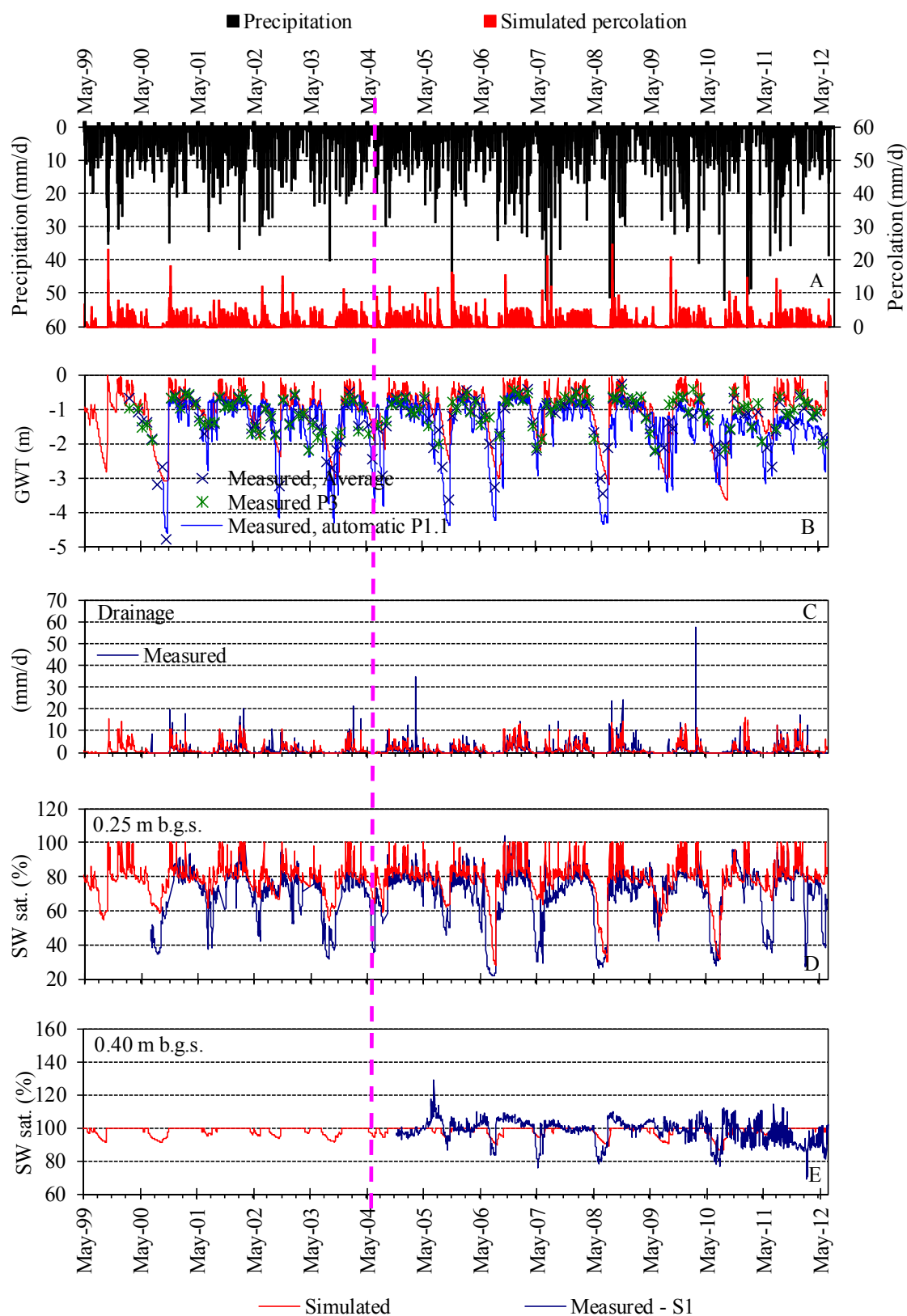
Figure 5.2. Soil water dynamics at **Estrup**: Measured precipitation and simulated percolation 0.6 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil saturation (SW sat.) at two different soil depths (D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in D and E derive from TDR probes installed at S1 (Figure 5.1). The broken vertical line indicates the beginning of the validation period (July 2004-June 2012).

Table 5.1. Annual water balance for **Estrup** (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation[2]	Precipitation	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge[3]
1.7.99–30.6.00[1]	968	1173	466	–	553	154[4]
1.7.00–30.6.01	968	887	420	356	340	111
1.7.01–30.6.02	968	1290	516	505	555	270
1.7.02–30.6.03	968	939	466	329	346	144
1.7.03–30.6.04	968	928	499	298	312	131
1.7.04–30.6.05	968	1087	476	525	468	86
1.7.05–30.6.06	968	897	441	258	341	199
1.7.06–30.6.07	968	1365	515	547	618	303
1.7.07–30.6.08	968	1045	478	521	556	46
1.7.08–30.6.09	968	1065	480	523	362	62
1.7.09–30.6.10	968	1190	533	499	523	158
1.7.10–30.6.11	968	1158	486	210	341	462
1.7.11–30.6.12	968	1222	406	479	577	337

[1] *Monitoring started in April 2000.*
[2] *Normal values based on time series for 1961–1990 corrected to the soil surface.*
[3] *Groundwater recharge is calculated as precipitation minus actual evapotranspiration minus measured drainage.*
[4] *Where drainage flow measurements are lacking, simulated drainage flow was used to calculate groundwater recharge.*

The simulated drainage (Figure 5.2C) matched the measured drainage flow quite well during fall 2010. Drainage flow measured in connection with snowmelt was either not captured by MACRO as on the 11 December 2010 or overestimated in magnitude during spring 2011. In the latter case the initiation of fluctuations in the drainage flow was captured. The periods preceding these drainage periods can be characterised by frozen soil and precipitation in the form of snow − a situation which MACRO has difficulties in describing. Drainage runoff over the whole monitoring period was high compared to that of the other two till sites investigated in the PLAP. This was due to a significantly lower permeability of the C-horizon than of the overlying A and B horizons (see Kjær *et al.* (2005c) for details).

The resulting water balance for Estrup for the entire monitoring period is shown in Table 5.1. Compared with the previous 12 years, the latest hydraulic year July 2011-June 2012 was characterized by having the second highest precipitation, the lowest simulated actual evapotranspiration during VAP and medium measured drainage. With MACRO not being able to capture drainage flow in connection with snowmelt resulted that the simulated drainage flow was largely overestimated. Precipitation in this year was characterized by July-September, December-January and June being very wet and November, February-Marts, and May being very dry (Appendix 4). Due to this precipitation pattern, the simulated percolation pattern of the year July 2011-June 2012 resulted in more or less continuously percolation during the hydrological year 2011-2012 (Figure 5.2A).
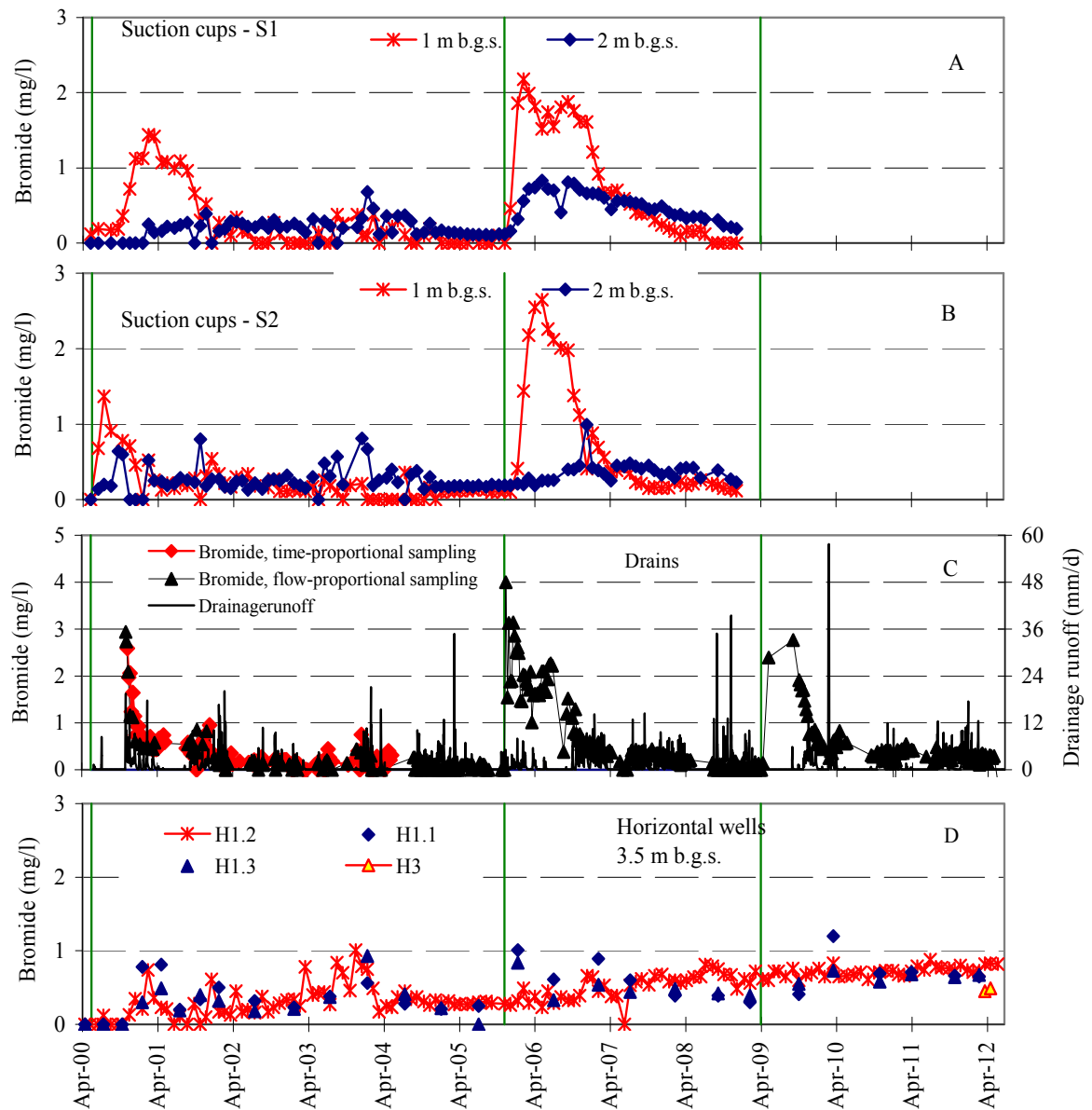
Figure 5.3. Bromide concentration at **Estrup**. A and B refer to suction cups located at S1 and S2, respectively. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring well H1 and H3 (D). In September 2008, bromide measurements in the suction cups were suspended (Appendix 2). The green vertical lines indicate the dates of bromide.

5.2.2 Bromide leaching

Bromide has now been applied three times at Estrup. The bromide concentrations measured up to October 2005 (Figure 5.3 and Figure 5.4) relate to the bromide applied in spring 2000, as described further in Kjær *et al.* (2003) and Barlebo *et al.* (2007). In March 2009, bromide measurements in the suction cups and monitoring wells M3 and M7 were suspended. Figure 5.3D show a very slow up building of bromide concentrations in the horizontal wells reflecting slow transport due to low hydraulic conductivity.
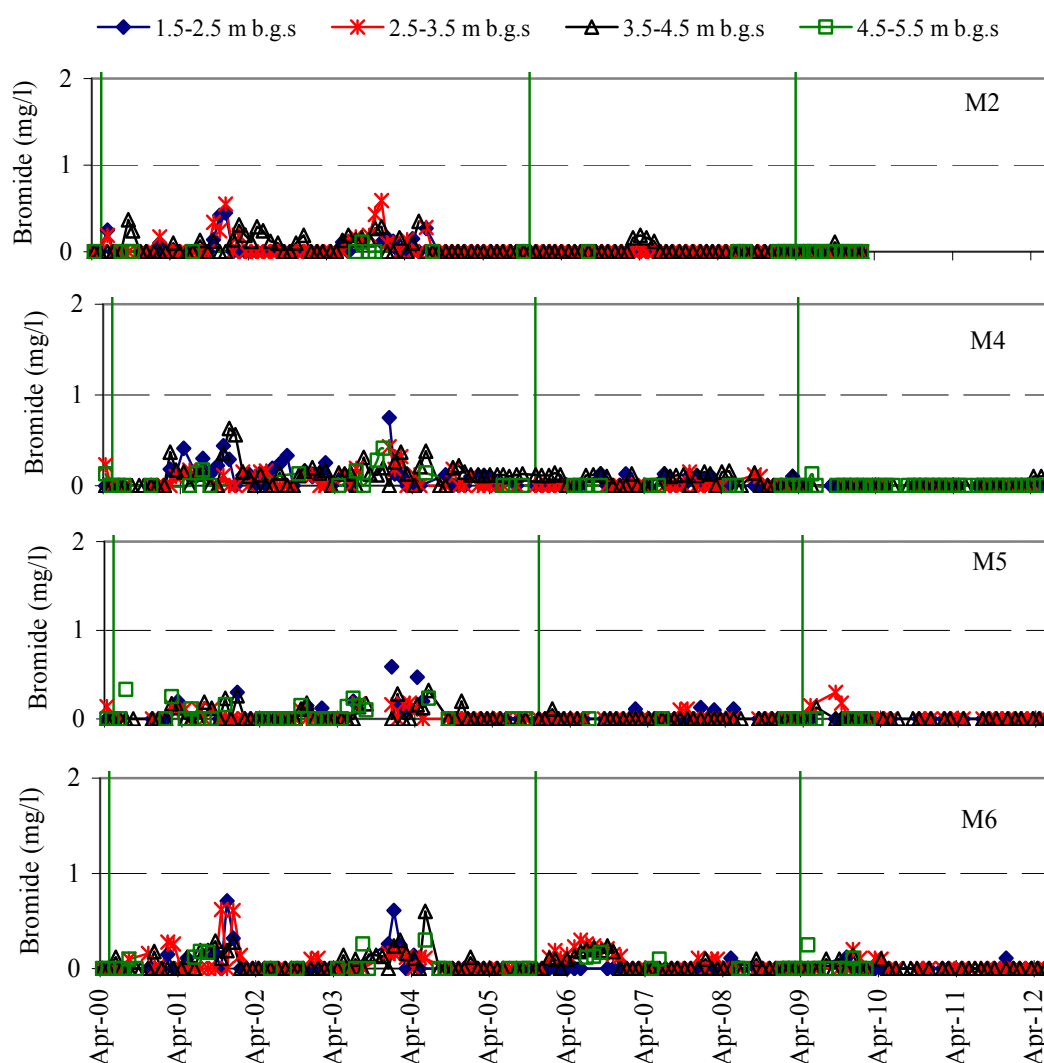
Figure 5.4. Bromide concentration at **Estrup**. The data derive from the vertical monitoring wells (M2–M6). Screen depth is indicated in m b.g.s. In September 2008, monitoring wells M3 and M7 were suspended (Appendix 2). The green vertical lines indicate the dates of bromide applications.

5.2.3   Pesticide leaching

Monitoring at Estrup began in May 2000. Pesticides and degradation products monitored so far can be seen from Table 5.2 (2007-2012) and Appendix 7, Table A7.4 (2000-2007). Pesticide application during the most recent growing seasons (2010/2011 and 2011/2012) is shown together with precipitation and simulated precipitation in Figure 5.5. It should be noted that precipitation is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (0.6 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model (Section 5.2.1). Moreover, pesticides applied later than April 2012 are not evaluated in this report and hence not included in Table 5.2.

Table 5.2. Pesticides analysed at **Estrup**. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Precip 1st year, Percol 1st year) and first mount (Precip 1st month, Percol 1st year) after the first application C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method, and Appendix 8 (Table A8.4) for previous applications of pesticides. (End monito.) end of monitoring of pesticide or metabolite.

Crop	Applied product	Analysed pesticide	Applica. Date	End Monito,	Y 1st precip	Y 1st percol	M 1st precip	M 1st percol	C_{mean}
Winter Wheat 2007	Atlantis WG	Mesosulfuron-methyl(P)	Oct 06	Jul 08	1420	305	90	29	0.01
		Mesosulfuron(M)	Oct 06	Jul 08	1420	305	90	29	<0.02
	Cycocel 750	Chlormequat(P)	Apr 07	Jul 08	1261	287	31	0	<0.01
	Opus	Epoxiconazole(P)	May 07	Jul 08	1154	299	154	29	0.02
Winter Wheat 2008	Amistar	Azoxystrobin(P)	Jun 08	Jun 12*	1093	232	88	0	0.06
		CyPM(M)	Jun 08	Jun 12*	1093	232	88	0	0.48
	Folicur EC 250	Tebuconazole(P)	Nov 07	Mar 10	1325	275	103	31	0.44
	Pico 750 WG	Picolinafen(P)	Oct 07	Mar 10	1253	267	76	24	0.03
		CL153815(M)	Oct 07	Mar 10	1253	267	76	24	0.24
	Roundup Max	Glyphosate(P)	Sep 07	Jun 12*	1200	261	113	29	0.19
		AMPA(M)	Sep 07	Jun 12*	1200	261	113	29	0.13
Spring Barley 2009	Amistar	Azoxystrobin(P)	Jun 09	Jun 12*	1215	235	60	0	0.04
		CyPM(M)	Jun 09	Jun 12*	1215	235	60	0	0.41
	Basagran M75	Bentazone(P)	May 09	Jun 12*	1222	238	83	4	0.05
	Fox 480 SC	Bifenox(P)	May 09	Jun 12*	1243	246	87	16	<0.02
		Bifenox acid(M)	May 09	Jun 12*	1243	246	87	16	0.16
		Nitrofen(M)	May 09	Jun 12*	1243	246	87	16	<0.01
Winter Rape 2010	Biscaya OD 240	Thiacloprid(P)	May 10	Mar 12	1083	196	43	0	<0.01
		M34(M)	May 10	Mar 12	1083	196	43	0	<0.02
		Thiacloprid sulfonic acid(M)	May 10	Mar 12	1083	196	43	0	<0.1
		Thiacloprid-amide(M)	May 10	Mar 12	1083	196	43	0	<0.01
Winter Wheat 2011	Express ST	Triazinamin-methyl(M)[1]	Sep 10	Jun 12*	823	176	97	31	0.01
	Fox 480 SC	Bifenox(P)	Apr 11	Jun 12*	1217	276	45	2	<0.01
		Bifenox acid(M)	Apr 11	Jun 12*	1217	276	45	2	0.003
		Nitrofen	Apr 11	Jun 12*	1217	276	45	2	<0.01
	Flexity	Metrafenone(P)	May 11	Jun 12*	1219	283	114	6	0.02
Spring Barley 2012	Roundup Max	Glyphosate(P)	Oct 11	Jun 12*	754	212	94	26	0.88
		AMPA(M)	Oct 11	Jun 12*	754	212	94	26	0.26

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
[1]*Degradation product of tribenuron-methyl. The parent degrade rapidly to be detected by monitoring.*
*monitoring continues the following year.

The current report focuses on pesticides applied from 2010 and onwards, while leaching risk of pesticides applied in 2009 and before has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).
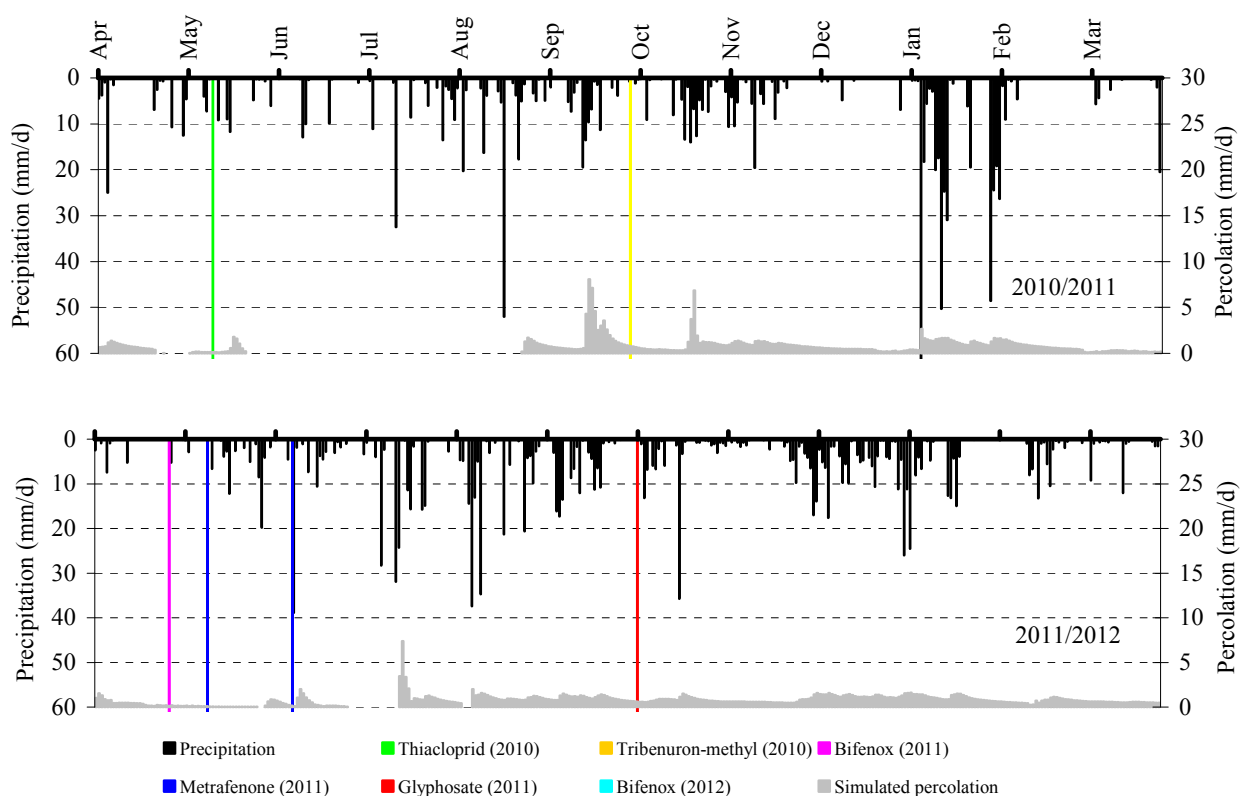
Figure 5.5. of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation 0.6 m b.g.s. (secondary axis) at **Estrup** in 2010/2011 (upper) and 2011/2012 (lower). The parent pesticide Tribenuron-methyl degrade to triazinamin-methyl, Table 5.2.

Azoxystrobin has now been applied four times at Estrup: 22 June 2004, 29 June 2006, 13 June 2008 and 4 June 2009 (Figure 5.6). The last application before these 4 was in June 1998 (Lindhardt *et al.*, 2001). Following all four applications azoxystrobin and the metabolite CyPM leached to the depth of the drainage system at the onset of drainage due to infiltration of excess rain. Concentrations in drainage water of both parent and metabolite are shown in Figure 5.6B and 5.6C. The maximum measured concentration of azoxystrobin was 1.4 µg/L on 24 August 2006 and 2.1 µg/L of CyPM on 11 September 2008.

Within the year of application as well as the following year, the average concentrations of CyPM in drainage water were higher than of azoxystrobin (Figure 5.6B and 5.6C), indicating its higher persistence. When drainage runoff commenced in the autumn of 2011, the third runoff season following the 2009 spraying, CyPM could still be found in concentrations above 0.1 µg/L, ranging between 0.022 and 0.29 µg/L. Differences in persistence for the two substances is further underlined by the fact that only two of 518 groundwater samples contained azoxystrobin (0.04 µg/L data not shown) whereas 15 contained CyPM, maximum concentration being 0.09 µg/L, Figure 5.6D and Table A5.4. The leaching pattern of azoxystrobin and CyPM is further described in Jørgensen et al., 2012a and Jørgensen et al., 2012b.
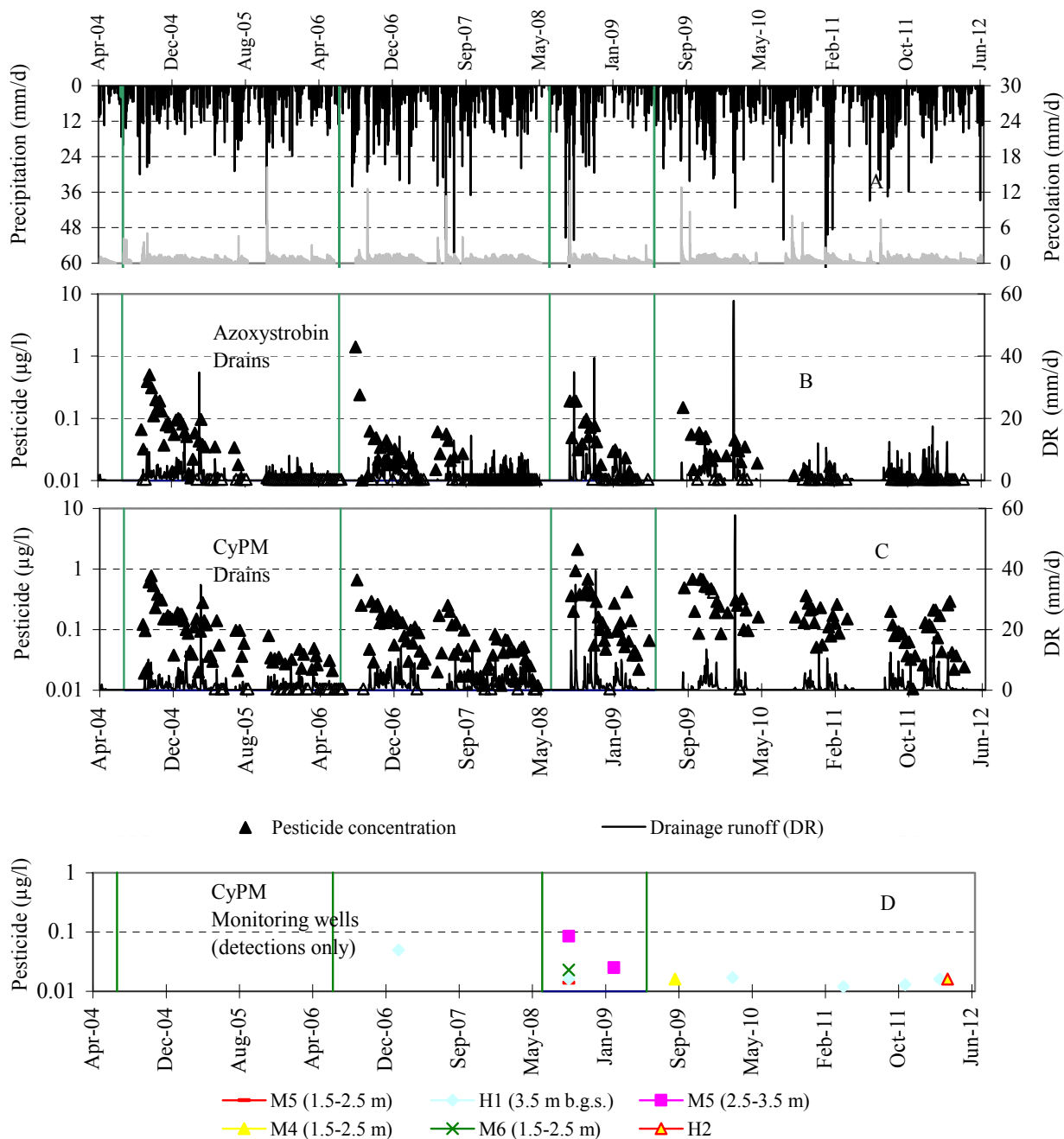
Figure 5.6. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff (DR on the secondary axis) at **Estrup**. Detections of CyPM in groundwater monitoring screen are indicated in D. Azoxystrobin was only detected once in groundwater horizontal and monitoring screens (see text). The green vertical lines indicate the dates of applications. Open symbols in B and C indicate values below the detection limit of 0.01 μg/L.

The herbicide bifenox was used on 1 May and on 30 September 2009 as well as on 26 April 2011. Both applications in 2009 caused leaching of bifenox to the drainage system reaching. A maximum of 0.15 μg/L was reached less than 2 weeks after the May application (data not shown, see Brüsch et al., 2013). The metabolite bifenox acid was leached to the drainage water following all three applications in concentrations larger than 0.1 μg/L, maximum being 1.9 μg/L on the 9 September 2009(data not shown). Neither bifenox nor bifenox acid was found in the groundwater monitoring screens and a second metabolite, nitrofen, neither in drain nor groundwater. The Danish EPA has prohibited the use of bifenox in Denmark on the base of data from the PLAP.

The herbicide glyphosate has now been applied at Estrup in 2000, 2002, 2005, 2007 and 2011 (Figure 5.7). Following all applications, both glyphosate and AMPA could be found in the drainage water. Out of 450 drainage water samples analysed for glyphosate and AMPA in the period 31 October 2000-7 March 2012, the concentrations of glyphosate and AMPA exceeded 0.1 µg/L in 104 and 111 samples, respectively (Figure 5.7B and 5.7C). During that period AMPA never exceeded 0.1 µg/L in groundwater (Figure 5.7E and Table A5.4 in Appendix 5), whereas glyphosate did so in four samples, of which two were taken on 7 July 2005 from two different wells, concentrations being 0.67 and 0.59 µg/L, one on 13 January 2010 from a third well with a concentration of 0.17 µg/L and one on from a horizontal well concentration 0.21 µg/L on 6 October 2011 (Figure 5.7D and Table A5.4 in Appendix 5). The results from the external quality assurance reveal that in the period June 2007 to July 2010 the concentration of glyphosate may have been underestimated by a factor of up to approximately 2 as compared to previous periods. A modification of the analytical procedure has been implemented in the analysis to address this problem (for further details see section 7.2.2).

When comparing the three-year periods following the application of glyphosate in September 2002 and the four year period following the September 2007 application, a pattern of longevity/persistence seems to emerge, in particular regarding AMPA (Figure 5.7B and Figure 5.7C). This long-term leaching of AMPA may indicate that AMPA is retained within the soil and gradually released over a very long time, as described in Kjær *et al.* (2005a), or that glyphosate is retained within the soil and then gradually degraded into AMPA. With an increased detection of glyphosate in the groundwater samples at Estrup following high precipitation events in September 2005 (nearly three years after latest application), September 2008 and January 2010 (one and two and a half years after the latest application, respectively), evidence of the latter pattern seems also to be recognizable.

It is remarkable that detections of particularly glyphosate in groundwater monitoring wells seem to increase over the years (Figure 5.7D). Within the first four years, detections of glyphosate were scarce, and AMPA was not found at all (Figure 5.7E). Following these four years there is an increase in the first 3 years, particularly in detections and concentrations of glyphosate. A similar tendency was observed for AMPA, although detections are less frequent and the concentrations comparatively lower. In this respect it should be noted that there had been no application of glyphosate for at least seven years prior to the 2000 application (Lindhardt *et al.*, 2001). A single detection in the most recent year, where there had not been sprayed, was of glyphosate, Figure 5.7D.

Thiacloprid, a pesticide, was applied on 10 May 2010. Neither samples of drainage nor groundwater have contained the pesticide or two of the metabolites, thiacloprid sulfonic acid (M30) or thiacloprid sulfonic acidamide (M34). Thiacloprimid-amide (M2) was found in one drainwater sample (0.012 µg/L).
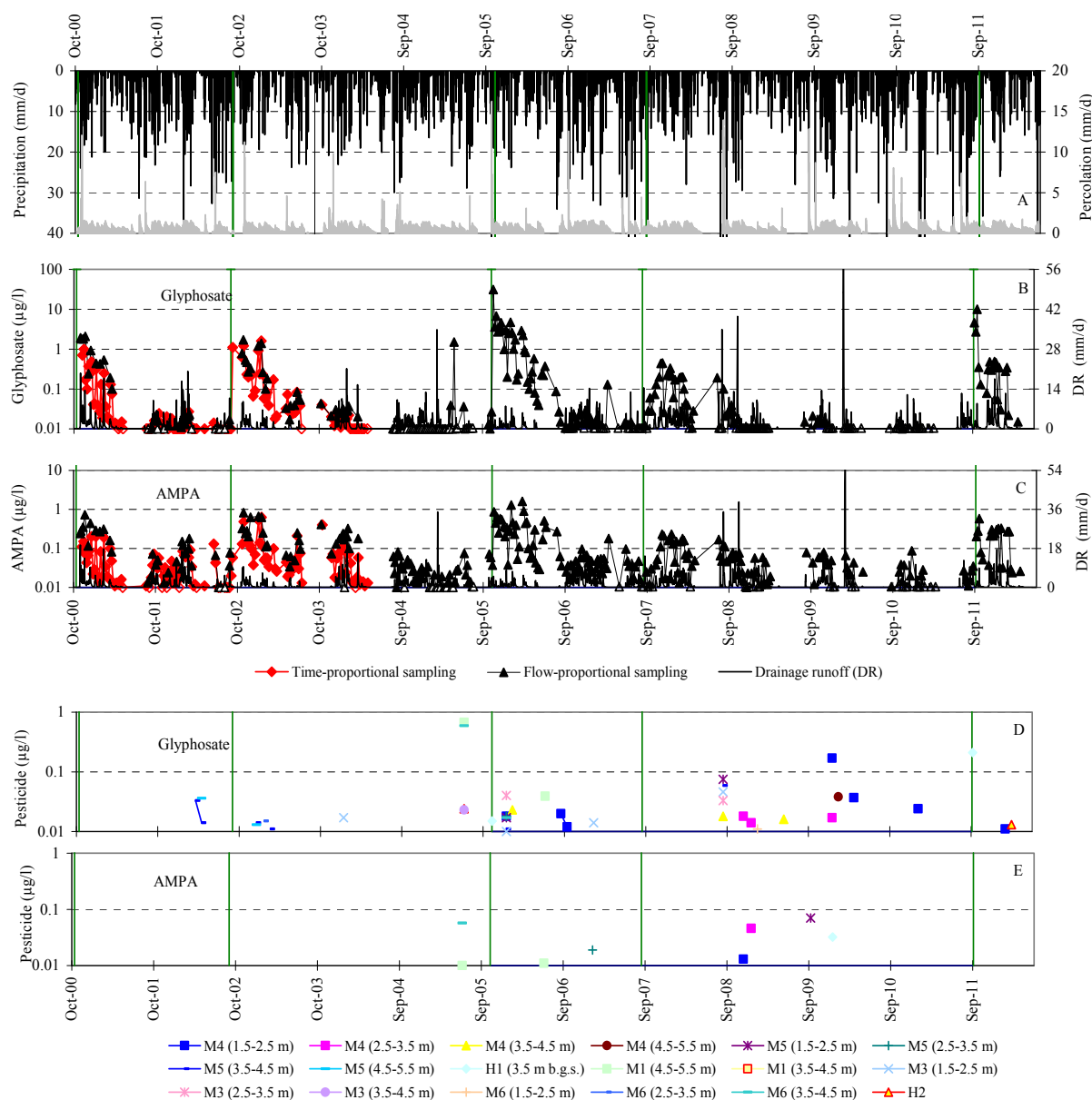
Figure 5.7. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with the concentration of glyphosate (B) and AMPA (C) in the drainage runoff (DR on the secondary axis) at **Estrup**. Data represent a x-year period including four applications of glyphosate as indicated by the green vertical lines. Open symbols indicate values below the detection limit of 0.01 µg/L. Detection of glyphosate and AMPA in groundwater monitoring wells is shown in D and E. In the period June 2007 until July 2010 analytical problems caused the concentration of glyphosate to be underestimated (see text for details).

Instead of the herbicide tribenuron-methyl, applied 30 September 2010 which degrades rapidly, its metabolite, triazinamin-methyl (INL5296) has been analyzed. The metabolite was not found in any of the 46 groundwater samples taken. However, it was detected in 2 out of 19 drainage water samples, concentrations being 0.042 µg/L on 28 October 2010 and 0.025 µg/L on 4 November 2010 (data not shown).

Pesticide leaching at Estrup is mostly confined to the depth of the drainage system. Apart from AMPA, CyPM, bentazone, desethyl-terbuthylazine, deisopropylatrazine, and glyphosate having been detected in 8, 11, 16, 7, 27 and 42 groundwater samples, respectively, pesticides have only sporadically been detected in groundwater monitoring

screens below the depth of the drainage system (Appendix 5, Table A5.4). Due to a very low hydraulic conductivity, and a lower degree of preferential flow, transport of water and solutes at Estrup is much slower beneath the drainage system than above it. Slow transport may allow for dispersion, dilution, sorption and degradation, thereby further reducing the deep transport. Compared to the other loamy soils investigated, the retention characteristics at Estrup suggest that the C-horizon (situated beneath the drainage depth) is less permeable with a lower degree of preferential flow occurring through macro pores (see Kjær *et al.*, 2005c, for details). An indication thereof are the long periods with groundwater table beyond drainage depth in which an increasing lateral transport to the drainage system and decreased leaching to the deeper groundwater will occur.

6 Pesticide leaching at Faardrup

6.1 Materials and methods

6.1.1 Site description and monitoring design

Faardrup is located in southern Zealand (Figure 6.1). The test field covers a cultivated area of 2.3 ha (150 x 160 m). The terrain slopes gently to the west by 1–3°. Based on three profiles in the buffer zone bordering the field, the soil was classified as Haplic Vermudoll, Oxyaquic Hapludoll and Oxyaquic Argiudoll (Soil Survey Staff, 1999). The topsoil is characterised as sandy loam with 14–15% clay and 1.4% organic carbon. Within the upper 1.5 m numerous desiccation cracks coated with clay are present. The test field contains glacial deposits dominated by sandy till to a depth of about 1.5 m overlying a clayey till. The geological description shows that small channels or basins filled with melt water clay and sand occur both interbedded in the till and as a large structure crossing the test field (Lindhardt *et al.,* 2001). The calcareous matrix and the reduced matrix begin at 1.5 m and 4.2 m b.g.s., respectively.

The dominant direction of groundwater flow is towards the west in the upper part of the aquifer (Figure 6.1). During the monitoring period the groundwater table was located 1–2 and 2–3 m b.g.s. in the lower and upper parts of the area, respectively. During fieldwork within the 5 m deep test pit it was observed that most of the water entering the pit came from an intensely horizontally-fractured zone in the till at a depth of 1.8–2.5 m. The intensely fractured zone could very well be hydraulically connected to the sand fill in the deep channel, which might facilitate parts of the percolation. The bromide tracer study showed that the applied bromide reached the vertical monitoring well (M6) located in the sand-filled basin (Figure 6.4), however, not in higher concentrations compared to concentrations detected water from other vertical monitoring wells. This indicate that the hydraulic contact with the surface in the "basin" does not differ from that in other parts of the test field, and that the basin is a small pond filled with sediments from local sources.

A brief description of the sampling procedure is provided in Appendix 2 and the analysis methods in Kjær et al. (2002). The monitoring design and test site are described in detail in Lindhardt et al. (2001). In September 2011, the monitoring system was extended with three horizontal screens (H3) 2 m b.g.s. in the South-Western corner of the field (Figure 6.1) - one of the screens should be located just below the drain 1.2 m b.g.s. A brief description of the drilling and design of H3 is given in Appendix 8.
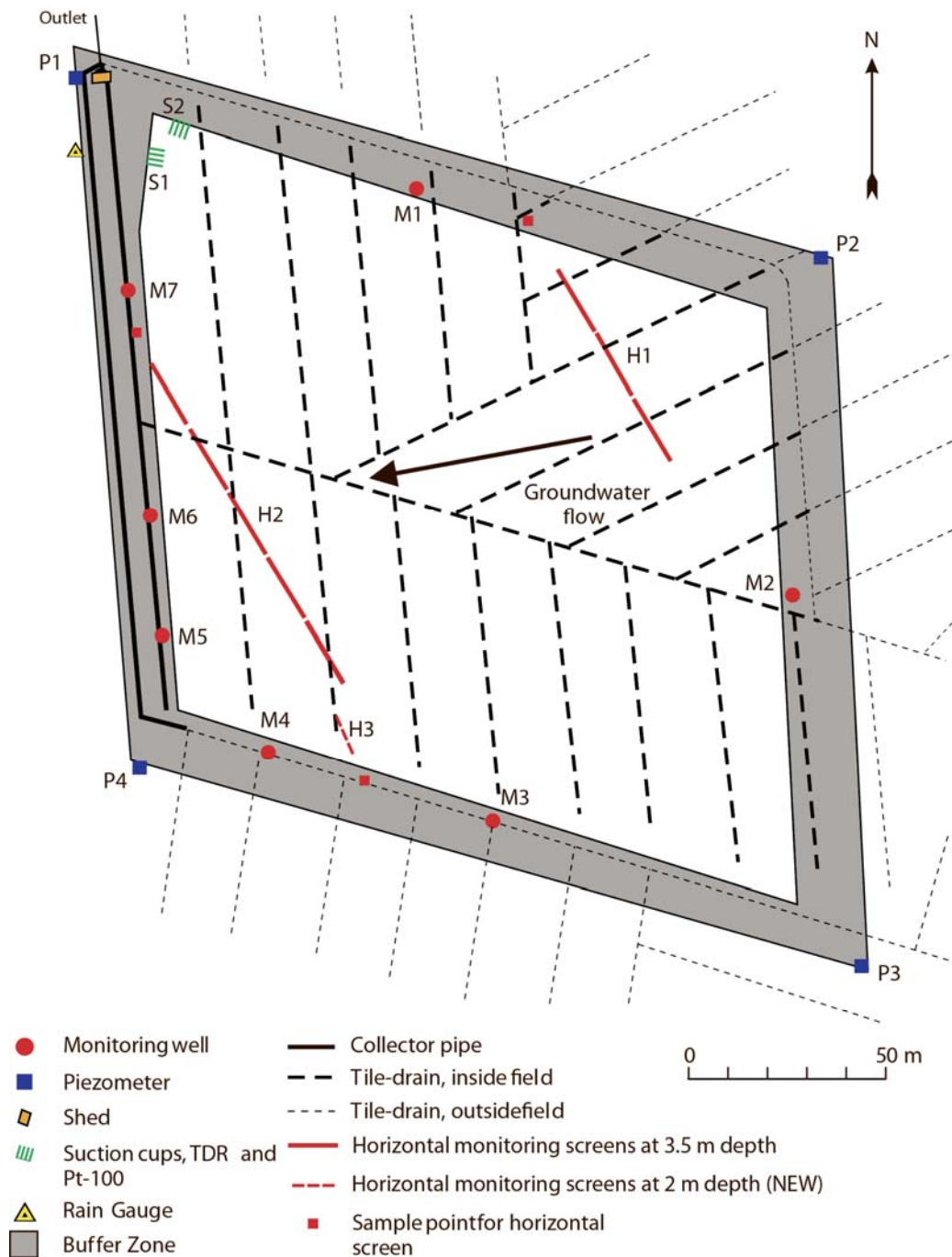
Figure 6.1. Overview of the **Faardrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted weekly from the drainage system (during period of continuous drainage runoff) and monthly and half-yearly from selected vertical and horizontal monitoring screens as described in Table A2.1 in Appendix 2.

6.1.2 Agricultural management

Management practice during the 2011-2012 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.5). For information about management practice during the previous monitoring periods, see previous monitoring reports available on http://pesticidvarsling.dk/publ_result/index.html.

The field, having a crop of red fescue (cv. Maximum) was sprayed with the herbicide fluazifop-P-butyl on the 21. May 2011. Having been windrowed on 5. July the crop was threshed on the 20 July yielding 7.2 hkg/ha of grass seed (87% dry matter), slightly less than the average for the year and soil type (Plantedirektoratet, 2011). An amount of 21.1 hkg/ha of straw, (100% dry matter) was removed at the day of harvest. Due to a poor grass stand it was decided to kill the crop using glyphosate on the 3. October. The field was subsequently ploughed on 8 November. On 4 April 2012 the field was sown with a mixture of spring barley varieties under sown with white clover (cv. Liflex) for clover seed production.

6.1.3 Model setup and calibration

The numerical model MACRO (version 5.1) was applied to the Faardrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model was used to simulate the water flow in the unsaturated zone during the full monitoring period September 1999-June 2012 and to establish an annual water balance.

Compared to the setup in Brüsch *et al.* (2013), a year of validation was added to the MACRO setup for the Faardrup site. The setup was accordingly calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2012. For this purpose, the following time series were used: observed groundwater table measured in the piezometers located in the buffer zone, water content measured at three depths (25, 60, and 110 cm b.g.s.) from the two profiles S1 and S2 (Figure 6.1) and measured drainage flow. Data acquisition and model setup are described in Barlebo *et al.* (2007).

Table 6.1. Annual water balance for **Faardrup** (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation[1]	Precipitation[2]	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge[3]
1.7.99–30.6.00	626	715	572	192	152	-50
1.7.00–30.6.01	626	639	383	50	35	206
1.7.01–30.6.02	626	810	514	197	201	99
1.7.02–30.6.03	626	636	480	49	72	107
1.7.03–30.6.04	626	685	505	36	19	144
1.7.04–30.6.05	626	671	469	131	55	72
1.7.05–30.6.06	626	557	372	28	16	158
1.7.06–30.6.07	626	796	518	202	212	77
1.7.07–30.6.08	626	645	522	111	65	12
1.7.08–30.6.09	626	713	463	46	20	204
1.7.09–30.6.10	626	624	415	54	43	155
1.7.10–30.6.11	626	694	471	133	184	90
1.7.11–30.6.12	626	746	395	98	106	252

[1] *Normal values based on time series for 1961–1990.*
[2] *For July 1999-June 2002, July 2003-June 2004, in January and February of both 2005 and 2006, and July 2006-June 2007, measured at the DIAS Flakkebjerg meteorological station located 3 km from the test site (see detailed text above).*
[3] *Groundwater recharge is calculated as precipitation minus actual evapotranspiration minus measured drainage.*

Due to electronic problems, precipitation measured at Flakkebjerg located 3 km east of Faardrup was used for the monitoring periods: July 1999-June 2002, July 2003-June 2004, January and February of both 2005 and 2006, and July 2006-June 2007. Precipitation measured locally at Faardrup was used for the rest of the monitoring period.

6.2   Results and discussion

6.2.1   Soil water dynamics and water balances

The level and dynamics of the soil water saturation in all three horizons in the hydraulic year July 2011-June 2012 were generally well described by the model (Figure 6.2D, 6.2E and 6.2F). However, for the summer period 2012 the model largely underestimated the drop in measured water saturation at 25 cm b.g.s. (Figure 6.2D).

The resulting water balance for Faardrup for the 13 monitoring periods is shown in Table 6.1. Compared with the previous 12 years, the latest hydraulic year July 2011-June 2012 was characterised by having the third highest precipitation, the third lowest simulated actual evapotranspiration, and the medium measured and simulated drainage. This results in the highest groundwater recharge estimated for this site within the PLAP-period. Precipitation in this year was characterised by July-October 2011 being very wet and November and Marts being very dry (Appendix 4). Due to this precipitation pattern, the duration of the simulated percolation period of the year July 2011-June 2012 was represented by continuous percolation throughout the period August-June (Figure 6.2A). Compared to the other years, the climate this year gave rise to long periods, where the groundwater table was just below drainage level, causing medium contributions to the drains (Figure 6.2B and 6.2C).
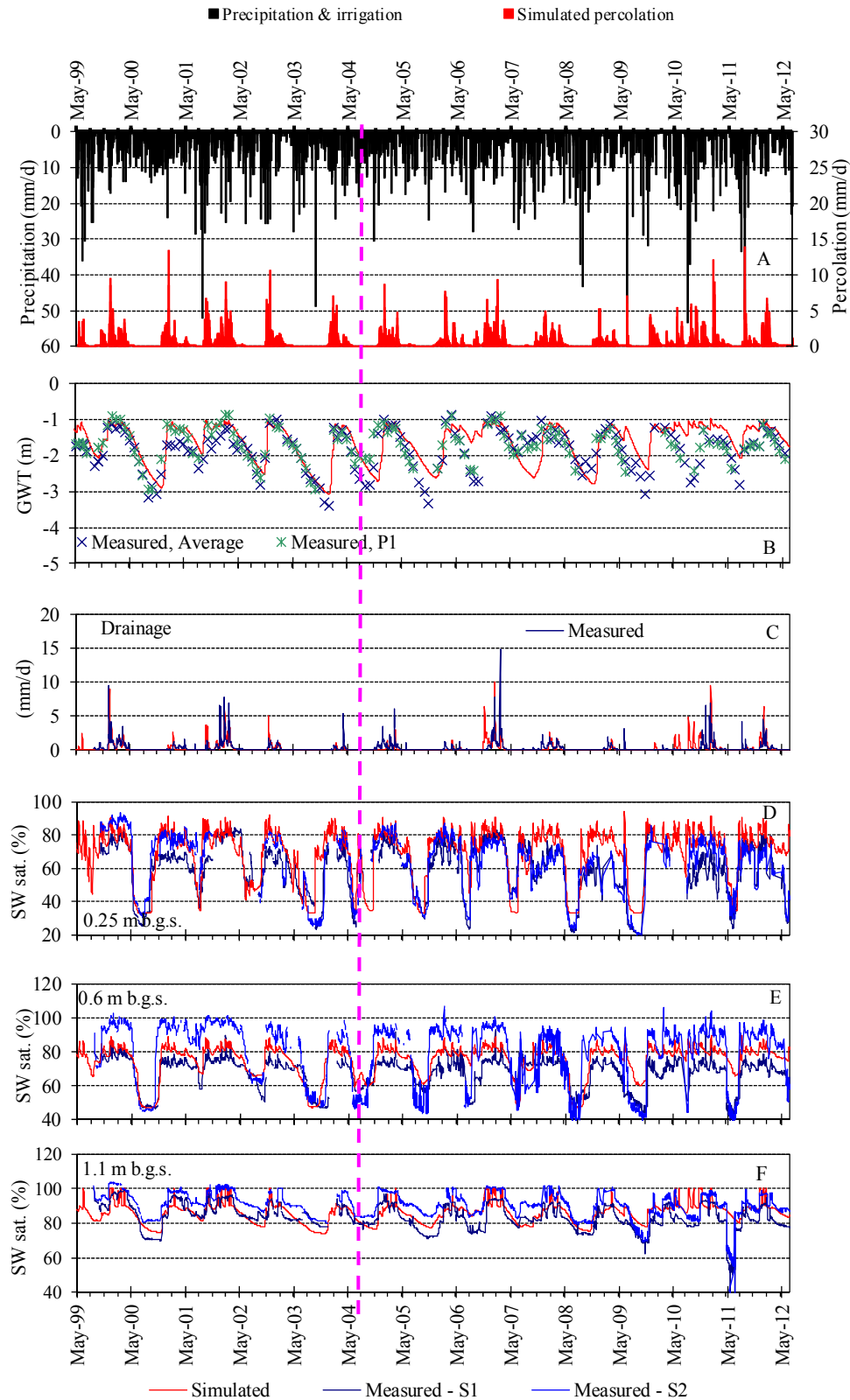
Figure 6.2. Soil water dynamics at **Faardrup**: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E, and F). The measured data in B derive from piezometers located in the buffer zone. The measured data in D, E, and F derive from TDR probes installed at S1 and S2 (Figure 6.1). The broken vertical line indicates the beginning of the validation period (July 2004-June 2012).
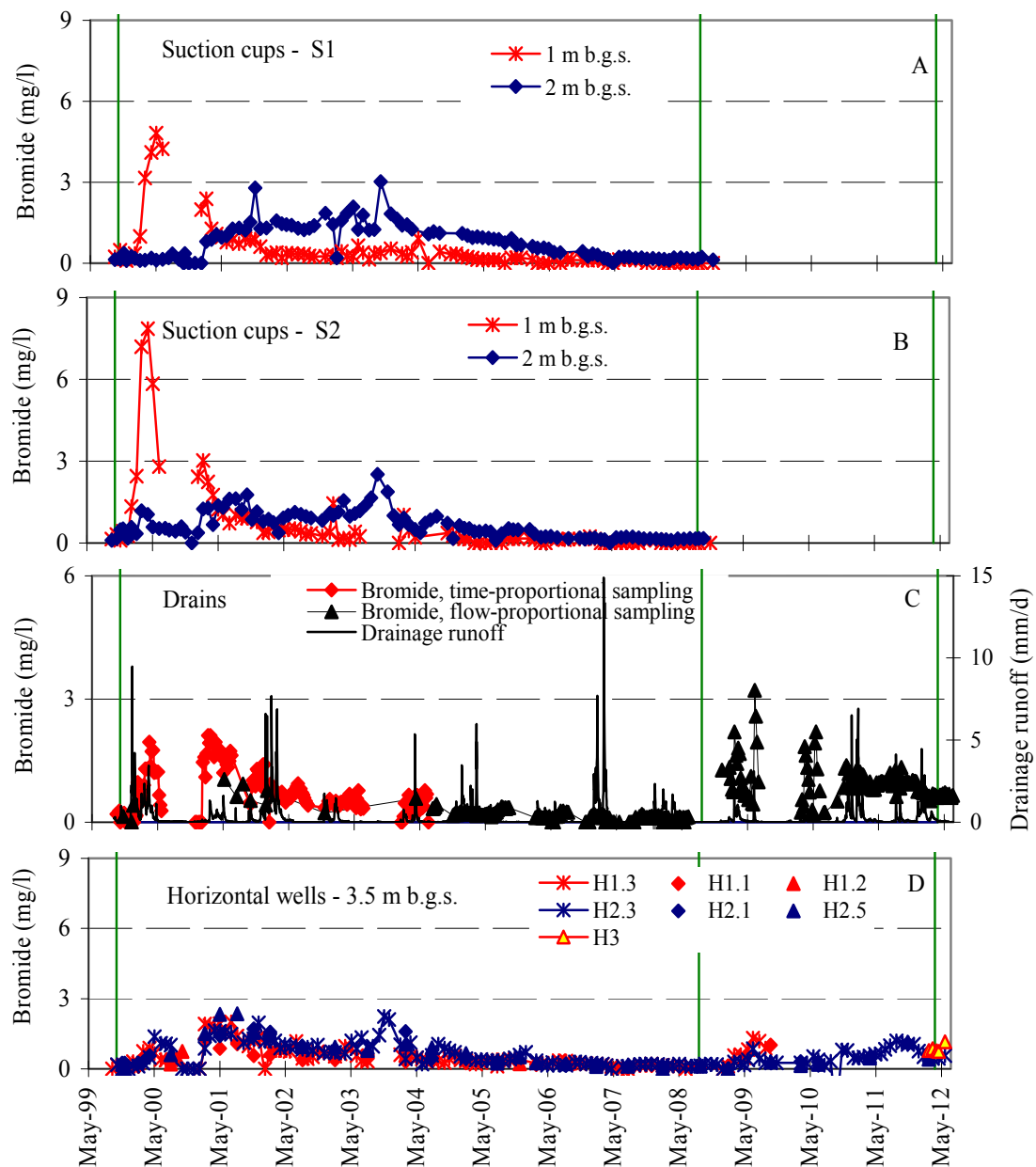
Figure 6.3. Bromide concentrations at **Faardrup**. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells (D). In September 2008, bromide measurements in the suction cups were suspended. The green vertical lines indicate the dates of bromide applications.

6.2.2 Bromide leaching

The bromide concentration shown in Figure 6.3 and Figure 6.4 relates primarily to the bromide applied in May 2000, as described further in Kjær *et al.* (2003), and further evaluated in Barlebo *et al.* (2007). In August 2008, 30 kg ha^{-1} potassium bromide was applied for the second time. In September 2008, bromide measurements in the suction cups and monitoring wells M2 and M7 were suspended. A drastic increase in bromide concentration in M4 and M5 was detected in May-June 2009 (Figure 6.4).
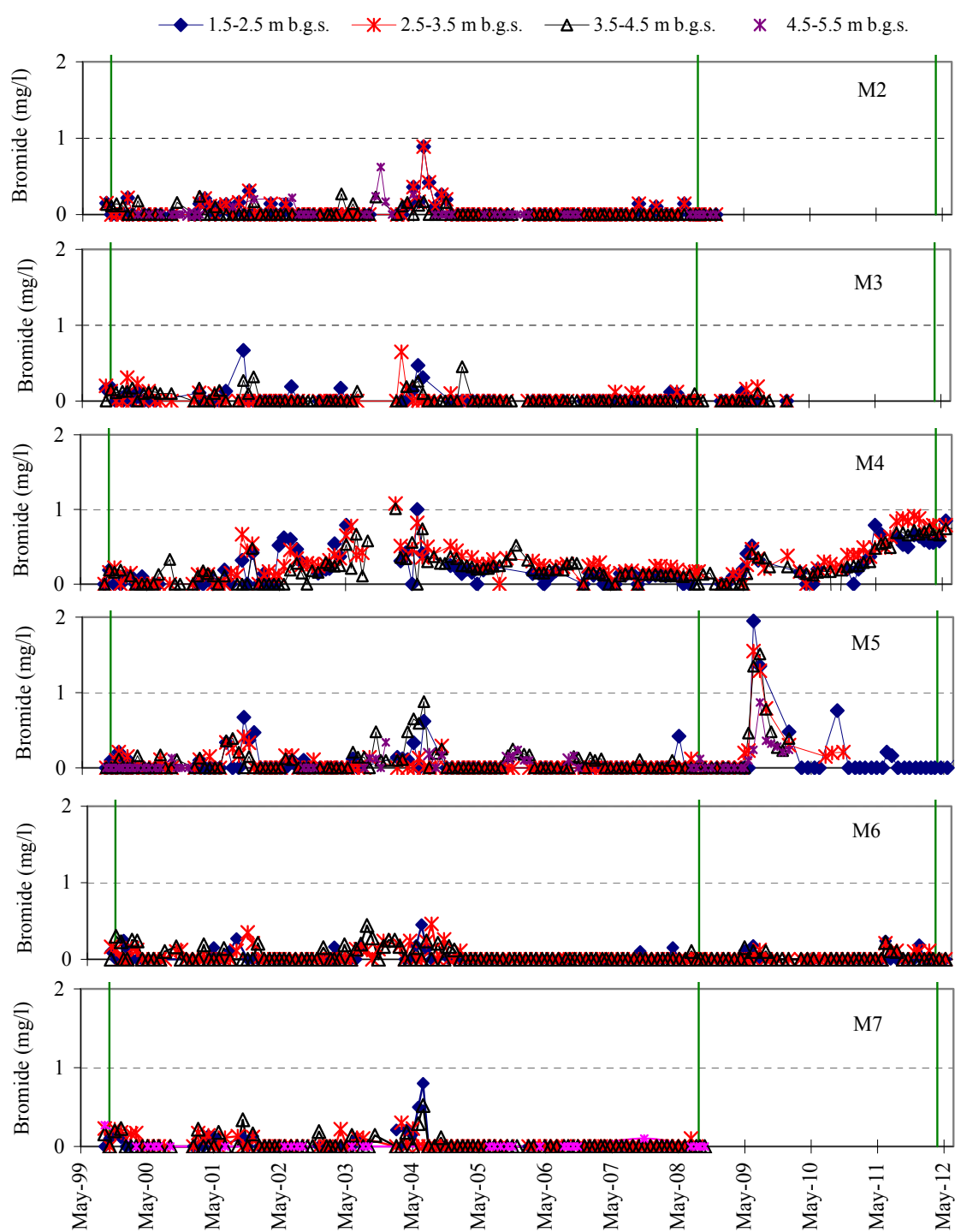
Figure 6.4. Bromide concentrations at **Faardrup**. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. In September 2008, monitoring wells M2 and M7 were suspended (Appendix 2). The green vertical line indicate the dates of bromide applications.
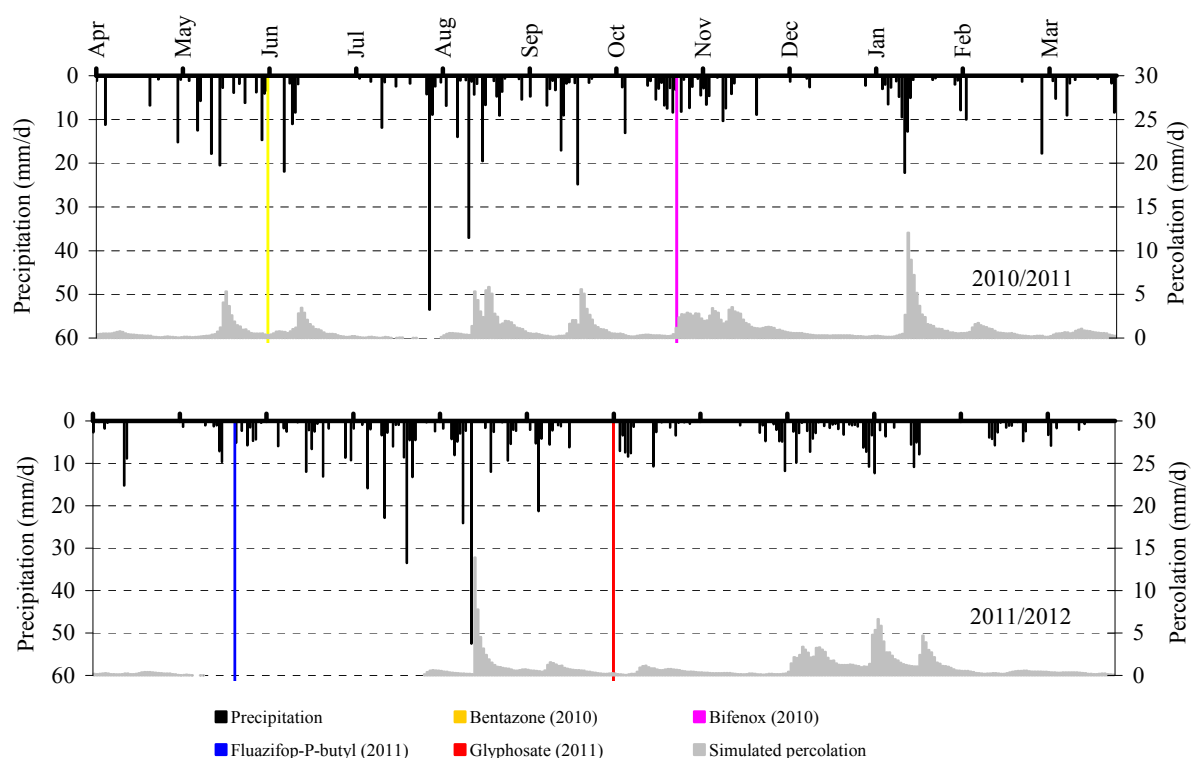
Figure 6.5. Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation (secondary axis) at **Faardrup** in 2010/2011 (upper), in 2011/2012 (lower).

6.2.3 Pesticide leaching

Monitoring at Faardrup began in September 1999 and presently encompasses several pesticides and their degradation products, as indicated in Table 6.2 and in Appendix 7, Table A7.5.

The application time of the pesticides included in the monitoring during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 6.5. It should be noted that precipitation is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated values as simulated with the MACRO model.

Table 6.2. Pesticides analysed at **Faardrup**. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Precip 1st year, Percol 1st year) and first mount (Precip 1st month, Percol 1st year) after the first application C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.5) for previous applications of pesticides. (End monito.) end of monitoring of pesticide or metabolite.

Crop	Applied product	Analysed pesticide	Applica. Date	End monito.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol	C_{mean}
Spring Barley 2006	Opus	Epoxiconazole(P)	Jun 06	Jun 08	790	306	17	3	<0.01
	Starane 180 S	Fluroxypyr(P)	May 06	Jun 08	708	333	37	17	<0.02
Winter Rape 2007	CruiserRAPS	Thiamethoxam(P)	Aug 06	Jun 08	806	294	57	23	<0.01
		CGA 322704(M)	Aug 06	Jun 08	806	294	57	23	<0.02
	Kerb 500 SC	Propyzamide(P)	Feb 07	Mar 09	735	199	64	46	0.01
		RH-24580(M)	Feb 07	Mar 09	735	199	64	46	<0.01
		RH-24644(M)	Feb 07	Mar 09	735	199	64	46	<0.01
		RH-24655(M)	Feb 07	Mar 09	735	199	64	46	<0.01
Winter Wheat 2008	Folicur 250	Tebuconazole(P)	Nov 07	Dec 09	693	158	64	56	<0.01
	Stomp SC	Pendimethalin(P)	Oct 07	Dec 09	673	180	51	24	<0.01
Sugar Beet 2009	Ethosan	Ethofumesate(P)	Apr 09	Jun 11	609	146	50	2	0.01
	Goliath	Metamitron(P)	Apr 09	Jun 11	609	146	42	2	0.02
		Desamino-metamitron(M)	Apr 09	Jun 11	609	146	42	2	0.06
	Safari	Triflusulfuron-methyl(P)	Apr 09	Jun 11	609	146	50	2	<0.01
		IN-D8526(M)	Apr 09	Jun 11	609	146	50	2	<0.01
		IN-E7710(M)	Apr 09	Jun 11	609	146	50	2	<0.01
		IN-M7222(M)	Apr 09	Jun 11	609	146	50	2	<0.02
Spring Barley and	Fighter 480	Bentazone(P)	Jun 10	Jun 12*	693	327	49	29	<0.01
Red Fescue 2010	Fox 480 SC	Bifenox(P)	Oct 10	Jun 12	351	190	75	72	0.02
		Bifenox acid(M)	Oct 10	Jun 12	351	190	75	72	2.54
		Nitrofen(M)	Oct 10	Jun 12	351	190	75	72	0.01
Red Fescue 2011	Fusilade Max	Fluazifop-P(M)	May 11	Mar 12	730	0	59	0	<0.01
	Fusilade Max	TFMP(M)	May 11	Jun 12*	730	0	59	0	<0.01
Spring Barley and	Glyphogan	Glyphosate(P)	Oct 11	Jun 12*	425	17	56	17	<0.01
White Clover 2011	Glyphogan	AMPA(M)	Oct 11	Jun 12*	425	17	56	17	<0.01
	Fighter 480	Bentazone(P)	May 12[1]	Jun 12*	99	4	29	4	<0.01
	Flexity	Metrafenone(P)	Jun 12[1]	Jun 12*	96	4	96	4	<0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
[1]*Application after April 2012.*
monitoring continues the following year.

The current report focuses on the pesticides applied from 2010 and onwards, while the leaching risk of pesticides applied before 2010 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

Bentazon, bifenox, fluazifop-P-butyl, and glyphosate have been applied on the Faardrup field during the hydrological years 2010/2011 and 2011/2012 (Table 6.2). The pesticides, except fluazifop-P-butyl, and the degradation products of:

- bifenox: bifenox-acid and nitrofen,
- fluazifop-P-butyl: fluazifop-P and TFMP
- glyphosate: AMPA

have all been included in the PLAP-monitoring programme for Faardrup. Bentazon, fluazifop-P, glyphosate, and AMPA have been tested in PLAP at Faardrup before 2010 (Appendix 7, Table A7.5).

In these two hydrological years, bentazon was applied to test its leaching potential in cereal with two different undersowings (bentazon is not allowed to be used in cereal without undersowning) – red fescue in 2010 and white clover 2012. The application onto spring barley and red fescue on the 1 June 2010 was followed by a very wet July-November 2010 resulting in bentazon to be detected after:

- 16 days in drainage water 1.2 m depth (0.11 µg/L)
- 23 days in water from 3.5 m depth (0.052 µg/L)
- 4 and 5 months in water from 3.5 m depth (0.028 µg/L and 0.012 µg/L)
- 5 and 6.5 months in drainage water 1.2 m depth (0.012 µg/L and 0.013 µg/L)

The application onto spring barley and white clover on the 18 May 2012 was followed by a dry period until the end of June (Appendix 5) and has not resulted in any detections of bentazon in the hydrological year 2011/2012.

Fluazifop-P-butyl has earlier (21 June 2001) been applied at Faardrup, but it has only been the degradation product fluazifop-P, which have been included in the PLAP-monitoring. This compound was found in few samples with max concentrations of 3.8 µg/L in drainage water and 0.17 µg/L in groundwater. The degradation product TFMP of fluazifop-P-butyl has, however, not been included in the PLAP-monitoring at Faardrup before May 2011. The reason for including it, was the TFMP-detections at Silstrup indicated a very high leaching potential of TFMP. These detections have resulted in a new admissible dose 50% lower (now 187.5 g active ingredient ha^{-1}) than the past application. Whether this reduced dose of fluazifop-P-butyl would result in negligible leaching of TFMP has now been under evaluation at Faardrup, where netprecipitation is 2/3 of the net precipitation at Silstrup. TFMP has not been detected yet at Faardrup.

Until 2011, glyphosate has only been applied at Faardrup as weed control both in August 1999 and October 2001. Third of October 2011, glyphosate was applied to desiccate the red ferscue. Compared to the earlier applications the dose was 1000 g active ingredient ha^{-1} higher (from 800 to 1800 g active ingredient ha^{-1}) and plant cover larger. After three days of no precipitation, 7 mm day^{-1} resulted in two detections of glyphosate in groundwater samples from the two upper filters in the down gradient vertical well M4 – both app. 0.02 µg/L. No extra detections were obtained in the hydrological year 2011/2012.

Bifenox has been applied to all three loamy soils included in PLAP during 2009/2010: Silstrup – September 2009 on red fescue; Estrup – May 2009 on spring barley; and Faardrup – October 2010 on spring barley and red fescue. At Faardrup, bifenox was detected in 6 water samples collected from drains from November 2010 to January 2011. The concentrations were below 0.1 µg/L (0.021-0.085 µg/L). Its degradation product bifenox-acid was found in 7 samples in 2010 from the drain, but in high concentrations from 0.23-6.9, and in one groundwater sample from the horizontal well H2 in a concentration of 0.19 µg/L (Figure 6.6). In January to August 2011 bifenox-acid was found in high, but decreasing concentrations in 11 water samples from the drain

(8.6 to 0.074 µg/L). The high detection limit is 0.05 µg/L for bifenox-acid should be noted. Like bifenox-acid, another degradation product nitrofen was detected in 5 drainwater samples in 2010 in concentrations from 0.014 to 0.16 µg/L and in one water sample from 2011 (0.018 µg/L).
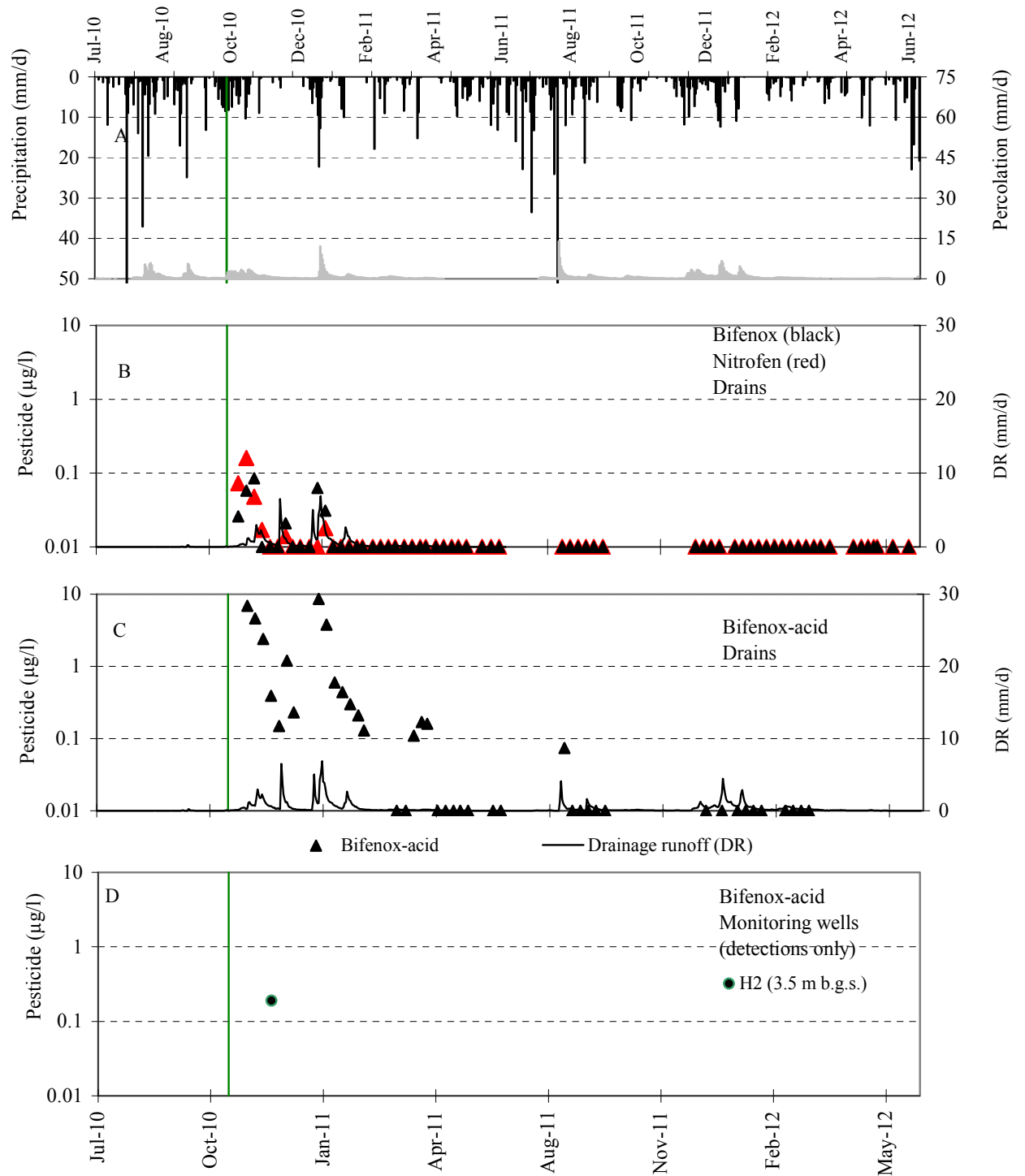
Figure 6.6. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with concentration of bifenox and nitrofen (B) and bifenox-acid (C) in the drainage runoff, and the detections of bifenox-acid (E) in the groundwater monitoring screens at **Faardrup**. The green vertical line indicate the date of bifenox application. Open symbols in B and C represent values below the detection limit of 0.01 µg/L (bifenox and nitrofen) and 0.05 µg/L (bifenox-acid).

7 Pesticide analysis quality assurance

Reliable results and scientifically valid methods of analysis are essential for the integrity of the present monitoring programme. Consequently, the field monitoring work has been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. Two types of sample are used in the quality control – samples with known pesticide composition and concentration are used for *internal monitoring* of the laboratory method, while *externally spiked samples* are used to incorporate additional procedures such as sample handling, transport and storage. Pesticide analysis quality assurance (QA) data for the period July 2011 to June 2012 are presented below, while those for the preceding monitoring periods are given in previous monitoring reports (available on http://pesticidvarsling.dk/publ_result).

7.1 Materials and methods

All pesticide analyses were carried out at a commercial laboratory selected on the basis of a competitive tender. In order to assure the quality of the analyses, the call for tenders included requirements as to the laboratory's quality assurance (QA) system comprising both an internal and an external control procedure. In addition to specific quality control under the PLAP, the laboratory takes part in the proficiency test scheme employed by the Danish Environmental Protection Agency when approving laboratories for the Nationwide Monitoring and Assessment Programme for the Aquatic and Terrestrial Environments (NOVANA).

7.1.1 Internal QA

With each batch of samples the laboratory analysed one or two control samples prepared in-house at the laboratory as part of their standard method of analysis. The pesticide concentration in the internal QA samples ranged between 0.03–0.10 µg/L. Using these data it was possible to calculate and separate the analytical standard deviation into within-day (S_w), between-day (S_b) and total standard deviation (S_t). Total standard deviation was calculated using the following formula (Wilson 1970, Danish EPA 1997):

$$s_t = \sqrt{s_w^2 + s_b^2}$$

7.1.2 External QA

Every four months, two external control samples were analysed at the laboratories along with the various water samples from the five test sites. Two stock solutions of different concentrations were prepared from standard mixtures in ampoules prepared by Dr. Ehrenstorfer, Germany (Table 7.1). Fresh ampoules were used for each set of standard solutions. The standard solutions were prepared two days before a sampling day and stored in darkness and cold until use. For the preparation of stock solutions 150 µl (low level) or 350 µl (high level) of the pesticide mixture was pipetted into a preparation glass containing 10 ml of ultrapure water. The glass was closed and shaken thoroughly and shipped to the staff collecting samples on the field locations. The staff finished the preparation of control samples in the field by quantitatively transferring the standard solution to a 3.0 l measuring flask. The standard solution was diluted and adjusted to the mark with groundwater from a groundwater well. After a thorough mixing, the control sample was transferred to a sample bottle similar to the monitoring sample bottles and transported to the laboratories together with the regular samples.

In the present report period the final concentrations in the solutions shipped for analysed in the laboratories were in the range 0.050 to 0.070 µg/L for low level spikes and 0.117 to 0.163 µg/L for high spike levels. As water sample supply was occasionally limiting at Faardrup, all volumes were reduced by a factor of three for this location, keeping the concentrations in the final control samples identical to the other locations.

The pesticide concentration in the solution is indicated in Table 7.1. Blank samples consisting of HPLC water were also included in the external QA procedure every month. All samples included in the control sample were labelled with coded reference numbers, so that the laboratory was unaware of which samples were controls or blanks.

Table 7.1. Pesticide concentrations in both the original ampoules and in the resulting high-level and low-level external control samples used in in the period 1.7.2011-30.6.2012.

Compound	Ampoule concentration (µg/L)	Ampoule	High-level control (µg/L)	Low-level control (µg/L)
AMPA	1000	2	0.117	0.050
Aclonifen	1000	1	0.117	0.050
Bentazone	1000	1	0.117	0.050
Bifenox acid	1400	1	0.163	0.070
Boscalid	1000	1	0.117	0.050
CGA 62826	1000	1	0.117	0.050
CyPM	1000	1	0.117	0.050
Cyazofamid	1000	1	0.117	0.050
Diflufenican	1000	1	0.117	0.050
Glyphosate	1000	2	0.117	0.050
Mesosulfuron-methyl	1000	1	0.117	0.050
Metrafenone	1000	1	0.117	0.050
PPU	1000	1	0.117	0.050
TFMP	1000	1	0.117	0.050
Thiacloprid-amide	1000	1	0.117	0.050
Triazinamin-methyl	1000	1	0.117	0.050

7.2 Results and discussion

7.2.1 Internal QA

Ideally, the analytical procedure provides precise and accurate results. However, in the real world results from analysis are subject to a certain standard deviation. Such standard deviation may be the combined result of several contributing factors. Overall, the accuracy of an analytical result reflects two types of error: Random errors related to precision and systematic errors relating to bias. In a programme like PLAP it is relevant to consider possible changes in analytical "reliability over time". As random and systematic errors may both change over time it is relevant to distinguish between standard deviations resulting from *within-day* variation as opposed to those associated with *between-day* variation in the analytical result. To this end, control samples are included in the analytical process as described above. Thus, by means of statistical analysis of the internal QA data provided by the laboratory it is possible to separate and estimate the different causes of the analytical variation in two categories: *day-to-day* variation and *within-day* variation (Miller *et al.,* 2000; Funk *et al.,* 1995). This kind of analysis can provide an indication of the reliability of the analytical results used in the PLAP. The statistical tool used is an analysis of variance (ANOVA) and encompasses all duplicate QA pesticide analyses, single analyses being excluded. The analysis can be divided into three stages:

1. **Normality**: An initial test for normality is made as this is an underlying assumption for the one-way ANOVA.

2. **Between-day contribution:** Explained simply, this test will reveal any day-to-day contribution to the variance in the measurements. If there is none, the total standard deviation can be considered to be attributable to the within-day error of the analysis. For this purpose an ANOVA-based test is used to determine if the between-day standard deviation (S_b) differs significantly from 0 (this test is made as an F-test with the $H_{0:}$ between-day mean square = within-day mean square).

3. **Calculating standard deviations:** If the F-test described above reveals a contribution from the between-day standard deviation (S_b), it is relevant to calculate three values: The within-day standard deviation (S_w), the between-day standard deviation (S_b), and the total standard deviation (S_t).

As the error associated with the analytical result is likely to be highly dependent on the compound analysed, the QA applied is pesticide-specific. In the current reporting period internal quality data was available for 32 compounds. The results of the internal QA statistical analysis for each pesticide are presented in Table 7.2. For reference, estimated S_b values are listed for all pesticides, including those for which the between-day variance is not significantly greater than the within-day variance. ANOVA details and variance estimates are also included, even for pesticides where the requirement for normality is not fulfilled. Obviously, such data should be interpreted with caution. Considering all compounds the mean variation S_w was 0.005, S_b 0.013 and S_b was 0.015, levels that are considered very suitable when relating to the residue limit for pesticides (0.1 µg/L).

As a rule of thumb, the between-day standard deviation should be no more than double the within-day standard deviation. From Table 7.2 it can be seen that S_b/S_w ratios greater than two were observed for several compounds. For these compounds, the results indicate that day-to-day variation makes a significant contribution. Among the compounds meeting the normality requirement, 8 out of 14 compounds had ratios above 2, and the highest S_b/S_w ratio in this group was observed for aminopyralid (8.0) and MNBA (mesotrione) 7.4, and these are rather high ratios. The cause differs for the two compounds.

For aminopyralid both S_b and S_w are small walues, actually indicating a analytical procedure in good control. For MNBA the high S_b/S_w ratio seems to be caused by a rather high S_w indicating that it may be possible to improve the analytical procedure for this compound to bring down the day to day variation. In previous reports high S_b/S_w ratio was observed for diflufenican, and in this reporting period the S_b/S_w ratio is still rather high (3.2). When all compounds are considered, high S_b/S_w ratio is also apparent for boscalid (9.2) and aclonifen (7.0). In previous reports high S_b/S_w ratio was observed for diflufenican, CGA 108906, PPU-desamino and PPU. In the current reporting period the S_b/S_w ratio is still rather high for diflufenican (3.2), CGA 108906 (5.3) and PPU-desamino (4.25) whereas the ratio seems to have improved for PPU (now 2.0, was 6.8, note normality criteria not met).

As for aminopyralid the relatively high S_b/S_w ratios can be caused by very low within-day standard deviations, i.e. within each laboratory day, the variation on the analysis is small compared to the other compounds, whereas the variation between days is comparable to the other compounds analysed. In contrast to aminopyralid this is not the case for the high ratio compounds MNBA and CGA 108906. For these compounds it is apparent that the high S_b/S_w ratio is caused by relatively high between-day deviation (S_b). The total standard deviation (S_t) of the various analyses of pesticides and degradation products lie within the range 0.003-0.0631 µg/L, the highest value being observed for MNBA (it should be noted that only 3 sets of QA data were available for this compound, so the result is considered tentative). In general, the data suggest that the analytical procedure used for the quantification of the compounds with high S_b/S_w ratio and/or high S_t may benefit from a critical review and possible optimisation of within day variation.

Table 7.2. Internal QA of pesticide analyses carried out in the period 1.7.2011-30.6.2012. Results of the test for normality, one-way analysis of variance (ANOVA), the estimated values of standard deviations (w: within-day, b: between-day, t: total – see text for details), pesticide concentration in internal QA sample (Conc.) and number of duplicate samples (n) are given for each pesticide. For test the P value α=0.05 was used.

Compound	Normal distribution α=0.05	Significant S_b Between day contribution ANOVA α=0.05	S_w (µg/L)	S_b (µg/L)	S_t (µg/L)	Ratio S_b/S_w	N	Conc. (µg/L)
AE-05422291*	-	-	0.002	0.006	0.006	3.3	12	0.05
AE-B107137*	-	-	0.013	0.020	0.024	1.5	11	0.10
AMBA*	yes	yes	0.020	0.020	0.028	1.0	4	0.10
AMPA*	-	yes	0.003	0.002	0.004	0.5	50	0.03
Aclonifen	-	-	0.002	0.011	0.011	7.0	13	0.05
Aminopyralid	yes	-	0.001	0.006	0.006	8.0	2	0.10
Azoxystrobin	-	-	0.003	0.011	0.011	3.9	37	0.05
Bentazone	-	-	0.003	0.010	0.011	3.6	38	0.05
Bifenox	-	-	0.004	0.011	0.012	3.0	51	0.05
Bifenoxacid*	yes	-	0.009	0.017	0.019	2.0	51	0.10
Boscalid	-	-	0.001	0.006	0.006	9.2	12	0.05
CGA108906*	-	-	0.004	0.021	0.022	5.3	13	0.10
CGA62826*	-	-	0.006	0.021	0.022	3.3	13	0.10
CyPM*	yes	-	0.004	0.006	0.007	1.5	24	0.05
Cyazofamid	-	-	0.002	0.009	0.010	4.0	11	0.05
Diflufenican	-	-	0.001	0.003	0.003	3.2	12	0.05
Fluazifop-P*	-	-	0.003	0.007	0.008	2.6	18	0.05
Glyphosate	-	-	0.002	0.002	0.003	1.3	50	0.03
M34*	-	-	0.008	0.046	0.047	5.7	35	0.10
MNBA*	yes	-	0.008	0.062	0.063	7.4	3	0.10
Mesotrione	yes	-	0.005	0.020	0.021	4.3	4	0.10
Metalaxyl-M	yes	-	0.001	0.004	0.004	3.1	13	0.05
Metrafenone	-	-	0.002	0.005	0.006	2.7	36	0.05
Nitrofen*	-	-	0.004	0.015	0.016	4.3	53	0.05
PPU*	yes	-	0.006	0.011	0.013	2.0	8	0.05
PPU-desamino*	yes	-	0.002	0.010	0.011	4.3	8	0.05
TFMP*	yes	-	0.004	0.006	0.007	1.8	42	0.05
Tebuconazole	yes	yes	0.001	0.003	0.003	2.7	2	0.05
Thiacloprid	-	-	0.005	0.015	0.015	3.2	33	0.05
Thiaclopridsulfonicacid*	yes	-	0.018	0.023	0.030	1.3	26	0.10
Thiacloprid-amide*	yes	-	0.003	0.009	0.010	2.7	33	0.05
Triazinamin-methyl*	yes	-	0.003	0.009	0.009	3.0	26	0.05

*Degradation product.

7.2.2 External QA

As described above the external QA program was based on samples spiked at the field sites. As part of the quality control a set of blanks made from HPLC water were also analysed to evaluate the possibility of false positive findings in the programme. From these results it can be concluded that contamination of samples during collection, storage and analysis is not likely to occur. In a total of 32 blank samples made from HPLC water no detection of the compounds analysed were made. As a consequence, samples analysed in the monitoring program and found to contain pesticides or degradation products are regarded as true positive findings.

Table 7.3. Externally spiked samples carried out in the period 1.7.2011-30.6.2012. Average recovery (%) of the nominal concentration at low/high concentration level is indicated for each site. For each compound n_{low} and n_{high} refer to the total number of samples being spiked at low and high concentrations, respectively. Bold font is used for recoveries outside the range 70% to 120%.

	Tylstrup %		Jyndevad %		Silstrup %		Estrup %		Faardrup %		Average %	$n_{low}/$ n_{high}
	Low	High	Low	High	Low	High	Low	High	Low	High		
AMPA							89	100	93	82	90	5/6
Aclonifen	**171**	**165**	120	**151**							152	6/6
Bentazone			**68**	**62**					98	100	90	4/4
Bifenox acid	71	85	75	61	82	73	79	76	85	77	76	8/11
Boscalid	118	120									119	3/3
CGA 62826	86	97	**160**	102							111	6/6
CyPM					**123**	120	**134**	120			125	5/5
Cyazofamid	93	89	90	104							94	6/6
Diflufenican			104	105	92	94					102	4/4
Glyphosate							94	105	107	73	94	5/6
Metrafenone							94	97	90	85	93	4/4
PPU	**38**	**32**	**220**	**140**							107	6/6
TFMP					102	97			88	88	93	6/6
Thiacloprid-amide							105	99			102	2/2
Triazinamin-methyl							78	75			77	3/3

Table 7.3 provides an overview of the recovery of all externally spiked samples. Since the results for each field site in Table 7.3 are based on only a few observations for each concentration level (high/low), the data should not be interpreted too rigorously.

A total of 42 samples were spiked in this reporting period, Whereas the recovery of the most spiked compounds in the samples is generally good (i.e. in the range 70% to 120%), the broad range of average recoveries indicates that for some compounds there may be reason for concern. Water used for spiking is taken on location from up-stream wells. For this reason a minor background content may be present in some of the water used for spiking, and in particular for low levels QC samples such content can cause an elevated recovery percentage. For this reason, the QC data must be considered as a whole, and used to keep track on possible changes in the quality of the program from period to period. In the present reporting period, the data points to the need for keeping track on particular compounds, i.e. aclonifen and PPU.

In previous reports somewhat low levels was observed for recovery of bifenox acid at Jyndevad and Estrup. In the present reporting period, such low recoveries were not observed, indicating that a more robust analytical method has been implemented in the program.

The previous reports have also pointed to possible recovery problems for PPU. In the current reporting period, low as well as high recoveries were observed, indicating that this compound is a challenge to quantify in the program.

Previous reports have discussed the QA for glyphosate and the initiatives that have been taken to improve the analysis of this compound. In the current reporting period the external spiked samples indicates good recovery.

All the compounds included in the spiking procedure (Table 7.1) were detected in the laboratory. Additionally, a number of compounds were measured at the threshold of detection of the analytical procedure (i.e. close to 0.01 µg/L). The occurrence of a

number of false positives is expected when analysing environmental matrices and these findings do not cause a general concern in relation to the reliability of the analytical procedures used in the programme.

At the sites Tylstrup and Jyndevad the compound PPU was frequently found at levels close to the detection limit, an observation that needs to be taken into consideration when evaluating the recovery data (Table 7.3). In the programme, the water matrix used for spiking was analysed. The high recovery of bifenox acid at Faardrup (170%) could not be explained by background content. In contrast, background content was observed at one occasion for the compound PPU (level 0.03 µg/L) and this can explain the rather high recovery observed for low level spiking of PPU at Jyndevad. However, in general, the analysis of the water used for spiking showed no or very low levels of background content (i.e. in the range of the detection limit) and these findings do not cause concern for the overall quality of the programme.

During the 2011/2012 monitoring period a total of six pesticides (azoxystrobin, bifenox, diflufenican, glyphosate, metalaxyl-M, metrafenone) and nine degradation products (AE-B107137, AMPA, bifenox acid, CGA 108906, CGA 62826 CyPM, nitrofen, PPU, PPU-desamino, TFMP, thiacloprid-amide) were detected in samples from the experimental fields. The external and internal QA data relating to these particular pesticides/degradation products are of special interest. These data (when available) are illustrated in Appendix 6.

7.3 Summary and concluding remarks
The QA system showed that:

- The internal QA indicates that the reproducibility of the pesticide analyses was good with total standard deviation (S_t) in the range 0.003-0.0631 µg/L.

- As demonstrated by the external QA, recovery was generally good in externally spiked samples. Relatively extreme recoveries indicated possible problems for PPU, but these findings may also be related to content of this compound in the water use for spiking at the field sites. Based on the results from analysis of blank 'HPLC water samples' shipped together with the true monitoring samples it is concluded that contamination of samples during collection, storage and analysis is not likely to occur.

8 Summary of monitoring results

This section summarizes the monitoring data from the entire monitoring period, i.e. both data from the two most recent monitoring years (detailed in this report) and data from the previous monitoring years (detailed in previous reports available on http://pesticidvarsling.dk/publ_result/index.html). Pesticide detections in samples from the drainage systems, suction cups and monitoring wells are detailed in Appendix 5. The monitoring data in 1 m b.g.s. (collected in drains and suction cups) reveal that the applied pesticides exhibit three different leaching patterns – no leaching, slight leaching and pronounced leaching (Table 8.1). Pronounced leaching in 1 m b.g.s. is defined as root zone leaching (1 m b.g.s.) exceeding an average concentration of 0.1 µg/L within the first season after application.

On sandy and loamy soils, leaching is determined as the weighted average concentration in soil water and drainage water, respectively (Appendix 2).

The monitoring data from the groundwater monitoring screens is divided into three categories: no detection of the pesticide (or its degradation products), detections of the pesticide (or its degradation products) not exceeding 0.1 µg/L, and detections of the pesticide (or its degradation products) exceeding 0.1 µg/L (Table 8.3). It should be noted, though, that the present evaluation of the leaching risk of some of these pesticides is still preliminary as their potential leaching period extends beyond the current monitoring period. Up to 2012 16 of the applied pesticides (or their degradation products) exhibited pronounced root zone leaching and 16 pesticides and degradation products were also detected in the groundwater monitoring screens in concentrations exceeding 0.1 µg/L.

- Azoxystrobin, and in particular its degradation product CyPM, leached from the root zone (1 m b.g.s.) in high average concentrations at the loamy sites Silstrup and Estrup. CyPM leached into the drainage water in average concentrations exceeding 0.1 µg/L at both the Silstrup and Estrup sites, while azoxystrobin only leached in concentrations exceeding 0.1 µg/L at Estrup (Table 8.1 and 8.2). At both sites, leaching of azoxystrobin and CyPM has hitherto mostly been confined to the depth of the drainage system, and they have rarely been detected in monitoring screens situated below drainage depth (Table 8.3 and 8.4). However, detection of CyPM in groundwater monitoring wells has gradually increased over time with highest numbers of detection found after the latest applications (2009 at Silstrup, Figure 4.7 and 2008 at Estrup, Figure 5.6). Apart from one sample, however, concentrations detected were all below 0.1 µg/L. In 2010 and 2011 CyPM continued to enter the drain water especially in Silstrup in high concentrations but in smaller concentrations in this monitoring year. At the loamy Faardrup site azoxystrobin and CyPM were detected in only four samples from the drainage water, and in no samples from the sandy Jyndevad site (Appendix 5).

Table 8.1. Leaching **1 m b.g.s**. of pesticides or their degradation products at the five PLAP sites. The colours indicate the degree of leaching. Pesticides applied in spring 2012 are not included in the table.

Risk	Parent	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
High	Azoxystrobin	Gray		Red	Red	Blue
	Bentazone		Red	Red	Red	Red
	Bifenox		Gray	Red	Red	Red
	Diflufenican*		Gray	Red		
	Ethofumesate			Blue	Red	Blue
	Fluazifop-P-butyl	Gray		Red		Blue
	Glyphosate			Red	Red	Blue
	Metalaxyl-M	Red	Red	Red		
	Metamitron			Blue	Red	Blue
	Metribuzin	Red	Red			
	Picolinafen				Red	
	Pirimicarb	Gray		Blue	Red	Blue
	Propyzamide			Red		Red
	Rimsulfuron	Blue	Red	Gray		
	Tebuconazole	Gray				Gray
	Terbuthylazine	Blue		Red	Red	Red
Low	Amidosulfuron		Blue			
	Bromoxynil	Gray	Gray		Blue	
	Clomazone	Gray				Blue
	Dimethoate	Gray		Blue	Gray	
	Epoxiconazole	Gray		Blue	Blue	Gray
	Flamprop-M-isopropyl			Blue	Blue	
	Fluroxypyr	Gray			Blue	
	Ioxynil	Gray	Gray		Blue	Gray
	MCPA	Gray			Blue	Blue
	Mancozeb	Blue				
	Mesosulfuron-methyl		Gray		Blue	
	Metrafenone				Blue	Gray
	Pendimethalin	Gray	Gray			Gray
	Phenmedipham	Gray		Gray		Blue
	Propiconazole	Gray	Gray	Blue	Blue	Gray
	Prosulfocarb			Blue		
	Pyridate		Gray	Blue		
	Triflusulfuron-methyl			Blue		Gray
None	Aclonifen	Gray				
	Aminopyralid				Gray	
	Boscalid					
	Chlormequat		Gray	Gray	Gray	Gray
	Clopyralid	Gray		Gray	Gray	
	Cyazofamid	Gray				
	Desmedipham	Gray		Gray		Gray
	Fenpropimorph	Gray	Gray			Gray
	Florasulam		Gray	Gray		Gray
	Iodosulfuron-methyl			Gray	Gray	
	Linuron	Gray				
	Mesotrione		Gray	Gray		
	Thiacloprid				Gray	
	Thiamethoxam	Gray		Gray	Gray	Gray
	Triasulfuron	Gray				Gray
	Tribenuron-methyl	Gray				Gray

■ (Red) Pesticide (or its degradation products) leached 1 m b.g.s. in average concentrations exceeding 0.1 µg/L within the first season after application.

■ (Blue) Pesticide (or its degradation products) was detected in either several (more than three) consecutive samples or in a single sample in concentrations exceeding 0.1 µg/L; average concentration (1 m b.g.s.) below 0.1 µg/L within the first season after application.

■ (Gray) Pesticide either not detected or only detected in very few samples in concentrations below 0.1 µg/L.

Will be reported in the next report.

Table 8.2. Number of samples from **1 m b.g.s**. in which the various pesticides and their degradation products were detected at each site with maximum concentration (µg/L) in parentheses. The table encompasses pesticides/degradation products detected in either several (more than three) consecutive samples or in a single sample in concentrations exceeding 0.1 µg/l. The pesticide and metabolites are mentioned if analyzed under compound. Pesticides applied in spring 2011 are not included. N (number of samples with detections). M (maximum concentration).

Risk	Parent	Analyte	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup	
			N	M	N	M	N	M	N	M	N	M
High	Azoxystrobin	Azoxystrobin	0	-	0	-	10	0.03	107	1.40	0	-
		CyPM	0	-	0	-	78	0.34	232	2.10	4	0.06
	Bentazone	2-amino-N-isopropyl-benzamide	0	-	2	0.03	0	-	1	0.06	1	0.06
		Bentazone	1	0.01	39	1.60	45	6.40	161	20.00	20	43.00
	Bifenox	Bifenox			2	0.04	5	0.38	3	0.15	6	0.09
		Bifenox acid			1	0.10	20	4.80	14	1.90	18	8.60
		Nitrofen			0	-	5	0.34	0	-	6	0.16
	Diflufenican	AE-B107137*			0	-						
		Diflufenican*			0	-						
	Ethofumesate	Ethofumesate					20	0.23	35	3.36	14	12.00
	Fluzifop-P-butyl	Fluzifop-P	0	-	0	-	0	-			9	3.80
		TFMP					29	0.64			0	-
	Glyphosate	AMPA			1	0.01	122	0.35	393	1.60	15	0.11
		Glyphosate			0	-	67	4.70	273	31.00	5	0.09
	Metalaxyl-M	CGA 108906	37	4.80	42	3.70						
		GCA 62826	15	0.11	40	1.20						
	Metamitron	Metalaxyl-M	4	0.03	10	0.04						
		Desomino-metamitron					58	0.67	49	5.55	16	2.50
		Metamintron					45	0.55	42	26.37	12	1.70
	Metribuzin	Desamino-diketo-metribuzin	63	2.10	0	-						
		Diketo-metribuzin	184	0.62	3	0.09						
	Picolinafen	CL 153815			0	-			31	0.50		
		Picolinafen			1	0.02			17	0.07		
	Pirimicarb	Pirimicarb	0	-	0	-	14	0.05	40	0.08	7	0.06
		Pirimicarb-desmethyl	0	-	1	0.01	1	0.05	0	-	6	0.05
	Propyzamide	Pirimicarb-desmethyl-formamido	0	-	0	-	0	-	26	0.38	3	0.04
		Propyzamide	0	-			23	1.60			4	0.51
		RH-24580	0	-			2	0.02			0	-
	Rimsulfuron	RH-24644	0	-			15	0.05			4	0.02
		RH-24655	0	-			0	-			1	0.02
		PPU	141	0.09	182	0.29	0	-				
		PPU-desamino	37	0.03	111	0.18	0	-				
	Tebuconazole	Tebuconazole	0	-	0	-			41	2.00	4	0.05
	Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	5	0.02			28	0.11	87	6.30	8	1.00
		Desethyl-terbuthylazine	2	0.01	20	0.06	108	1.08	146	8.20	89	8.30
		Desisopropylatrazine	17	0.04			43	0.04	71	0.44	25	0.36
		Hydroxy-terbuthylazine	1	0.04			26	0.04	88	0.99	21	0.58
		Terbuthylazine	0	-	0	-	60	1.55	112	11.00	41	10.00
Low	Amidosulfuron	Amidosulfuron			3	0.11	0	-	0	-		
	Bromoxynil	Bromoxynil	0	-	0	-	0	-	3	0.60	0	-
	Clomazone	Clomazone	0	-							1	0.28
		FMC 65317	0	-							1	0.30
	Dimethoate	Dimethoate	0	-	0	-	1	1.42	0	-	0	-
	Fluroxypyr	Fluroxypyr	0	-	0	-	0	-	3	1.40	1	0.19
	Epixiconazole	Epixiconazole	0	-	0	-	0	-	14	0.39	0	-
	Flamprop-M-isopropyl	Flamprop	0	-			7	0.10	13	0.03	1	0.09
		Flamprop-M-isopropyl	0	-			12	0.11	20	0.07	1	0.04
	Ioxynil	Ioxynil	0	-	0	-	0	-	20	0.25	1	0.01
	MCPA	2-methyl-4-chlorophenol			0	-	0	-	1	0.05	1	0.24
		MCPA			0	-	0	-	12	3.89	2	0.28
	Mancozeb	ETU	6	0.04								
	Mesosulturon-methyl	Mesosulfuron-methyl			0	-			13	0.06		
	Metrafenone	Metrafenone							18	0.07		
	Pendimethalin	Pendimethalin	0	-	0	-	14	0.06	4	0.04	2	0.04
	Phenmedipham	MHPC					0	-			2	0.19
	Propiconazole	Propiconazole	0	-	0	-	6	0.03	26	0.86	0	-
	Prosulfocarb	Prosulfocarb					5	0.18			0	-
	Pyridate	PHCP			0	-	4	2.69				
	Triflusulfuron-methyl	IN-E7710					5	0.01			0	-

Will be reported in the next report.

Table 8.3. Detections of pesticides and their degradation products in water samples from the groundwater monitoring screens at the five PLAP sites (see Table 8.4 for details). Pesticides applied in spring 2012 are not included in the table.

Risk	Parent	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
High	Azoxystrobin	gray		red	blue	gray
	Bentazone			red		red
	Bifenox		blue			
	Ethofumesate			blue	gray	red
	Fluazifop-P-butyl	gray		red		red
	Glyphosate		blue	blue	red	blue
	Metalaxyl-M	red				
	Metamitron			red	gray	red
	Metribuzin	red				
	Pirimicarb			blue		blue
	Propyzamide	gray		red		blue
	Rimsulfuron	blue	red			
	Tebuconazole	blue	blue		red	blue
	Terbuthylazine	blue		red	blue	red
Low	Dimethoate			blue	gray	gray
	Epoxiconazole		blue	gray		
	Flamprop-M-isopropyl			blue		
	Fluroxypyr	gray			blue	blue
	Ioxynil	gray			gray	blue
	MCPA		gray		blue	gray
	Mancozeb	blue				
	Phenmedipham			gray		blue
	Propiconazole	gray			blue	
	Prosulfocarb			blue		gray
	Pyridate	gray		blue		
	Triflusulfuron-methyl	gray		blue		gray
None	Aclonifen	gray				
	Aminopyralid		gray		gray	
	Amidosulfuron		gray			
	Boscalid	gray				
	Bromoxynil	gray			gray	gray
	Clomazone					gray
	Chlormequat		gray		gray	
	Clopyralid	gray				
	Cyazofamid		gray	gray		
	Desmedipham			gray		gray
	Diflufenecan	gray				
	Fenpropimorph	gray	gray			gray
	Florasulam		gray	gray	gray	
	Iodosulfuron-methyl			gray		
	Linuron	gray				
	Mesotrione		gray			
	Metrafenone			gray	gray	
	Metsulfuron-methyl	gray		gray		gray
	Pendimethalin	gray	gray	gray		gray
	Picolinafen				gray	
	Thiacloprid					
	Thiamethoxam	gray				gray
	Triasulfuron		gray	gray		
	Tribenuron-methyl	gray				gray

Pesticide (or its degradation products) detected in water samples from groundwater monitoring screens in concentrations exceeding 0.1 μg/L. [red]

Pesticide (or its degradation products) detected in water samples from groundwater monitoring screens in concentrations not exceeding 0.1 μg/L. [blue]

Pesticide (or its degradation products) not detected in water samples from the groundwater monitoring screens. [gray]

Table 8.4. Number of samples from the **groundwater monitoring screens** in which the various pesticides and/or their degradation products were detected at each site with the maximum concentration (µg/L) in parentheses (see Appendix 5 for further details). The parent pesticide and metabolites are mentioned if analysed under compound. Only pesticides with more than 3 detections at one site are included. Pesticides applied in spring 2011 are not included. N (number of samples with detections). M (maximum concentration).

Risk	Parent	Analyte	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup	
			N	M	N	M	N	M	N	M	N	M
High	Azoxystrobin	Azoxystrobin	0		0		0		2	0.04	0	
		CyPM	0	-	0	-	28	0.10	15	0.09	0	-
	Bentazone	2-amino-N-isopropyl-benzamide	0	-	0	-	0	-	1	0.03	0	-
		Bentazone	0	-	0	-	29	0.44	16	0.02	13	0.60
	Bifenox	Bifenox			2	0.05	5	0.10	0	-	0	-
		Bifenox acid			0	-	26	3.10	1	0.11	1	0.19
	Ethofumesate	Ethofumesate					5	0.04	0	-	31	1.40
	Fluzifop-P-butyl	Fluzifop-P	0	-	0	-	1	0.07			6	0.17
		TFMP	0	-	0	-	55	0.29			0	-
	Glyphosate	AMPA			2	0.02	15	0.08	8	0.07	2	0.03
		Glyphosate			0	-	4	0.03	45	0.67	5	0.03
	Metalaxyl-M	CGA 108906	128	1.50	123	2.70						
		CGA 62826	7	0.04	37	0.68						
		Metalaxyl-M	9	0.08	17	1.30						
	Metamitron	Desamino-metamitron					30	0.19	0	-	48	1.30
		Metamintron					29	0.17	0	-	24	0.63
	Metribuzin	Desamino-diketo-metribuzin	236	0.20	20	1.83						
		Diketo-metribuzin	453	0.55	26	1.37						
	Pirimicarb	Metribuzin	1	0.01	0	-						
		Pirimicarb	0	-	0	-	3	0.01	1	0.02	2	0.04
		Pirimicarb-desmethyl	0	-	0	-	0	-	0	-	3	0.04
		Pirimicarb-desmethyl-formamido	0	-	0	-	0	-	0	-	2	0.08
	Propyzamide	Propyzamide	0	-			9	0.14			1	0.03
		RH-24644	0	-			2	0.03			0	-
	Rimsulfuron	PPU	41	0.05	344	0.18						
		PPU-desamino	5	0.02	88	0.09						
	Tebuconazole	Tebuconazole	1	0.01	1	0.01			5	0.12	1	0.01
	Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	1	0.03			1	0.02	0	-	7	0.09
		Desethyl-terbuthylazine	0	-	27	0.02	161	0.14	7	0.05	66	0.94
		Desisopropylatrazine	1	0.01			4	0.05	27	0.03	60	0.04
		Hydroxy-terbuthylazine	0	-			0	-	0	-	34	0.07
		Terbuthylazine	0	-	0	-	36	0.12	1	0.02	51	1.90
Low	Dimethoate	Dimethoate	0	-	0	-	1	0.09	0	-	0	-
	Epoxiconazole	Epoxiconazole	0	-	1	0.01	0	-	0	-	0	-
	Flamprop-M-isopropyl	Flamprop-M-isopropyl	0	-			1	0.02	0	-	0	-
	Fluroxypyr	Fluroxypyr	0	-	0	-	0	-	1	0.06	1	0.07
	Ioxynil	Ioxynil	0	-	0	-			0	-	1	0.01
	MCPA	MCPA			0	-	0	-	1	0.02	0	-
	Mancozeb	ETU	2	0.02								
	Phenmedipham	MHPC					0	-			1	0.05
		Phenmedipham					0	-			2	0.03
	Propiconazole	Propiconazole	0	-	0	-	0	-	2	0.02	1	0.04
	Prosulfocarb	Prosulfocarb					1	0.03			0	-
	Pyridate	PHCP			0	-	14	0.31				
	Triflusulfuron-methyl	IN-M7222					1	0.05			0	-

- Bentazone leached through the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 µg/L in the drainage system at the loamy sites of Silstrup, Estrup, and Faardrup. Moreover, bentazone was frequently detected in the monitoring screens situated beneath the drainage system at Silstrup and Faardrup (Table 8.3 and 8.4). Apart from eight samples (4 from Silstrup in 2003 and 4 from Faardrup in 2005), however, the concentrations detected were all below 0.1 µg/L. At Estrup leaching was mostly confined to the depth of the drainage system and rarely detected in deeper monitoring screens (Appendix 5). On the sandy soils, bentazone leached at Jyndevad, but was only detected once 1 m b.g.s. at Tylstrup. At Jyndevad high concentrations (exceeding 0.1 µg/L) were detected in the soil water samples from

suction cups 1 m b.g.s. four months after application. Thereafter, leaching diminished, and bentazone was not subsequently detected in the monitoring wells. Although leached in high average concentrations (>0.1 µg/L) at four sites, bentazone was generally leached within a short period of time. Initial concentrations of bentazone were usually very high, but then decreased rapidly. In general, concentrations exceeding 0.1 µg/L were only found within a period of one to four months following the application. The degradation product 2-amino-N-isopropyl-benzamide was detected twice in the vadose zone at Jyndevad, once in drainage water at Estrup and Faardrup (Table 8.2), and once in water from a horizontal well at Estrup (Table 8.4).

- Bifenox acid (degradation product of bifenox) leached through the root zone and entered the drainage water system in average concentrations exceeding 0.1 µg/L at the loamy sites of Silstrup, Estrup and Faardrup. While leaching at Estrup seems to be confined to the depth of the drainage system, leaching to groundwater monitoring wells situated beneath the drainage system was observed at Silstrup, where concentrations exceeding 0.1 µg/L were observed up to six months after application. As in Silstrup and Estrup the metabolite bifenox acid was found in very high concentrations in drain water from Faardrup, in a yearly average concentrations 2.54 µg/L (Table 6.2). In 2011/2012 bifenox acid leached, but in small concentrations, and bifenox was only found in few water samples. Another unwanted metabolite from bifenox, nitrofen, was found in drain water from Faardrup, often in low concentrations, but in Silstrup, 0.34 µg/L was found in one drain water sample. Similar evidence of pronounced leaching was not observed on the coarse sandy soil as there was only a single detection of bifenox acid in soil water, whereas bifenox was detected very sporadically in soil and groundwater, concentrations always less than 0.1 µg/L.

- In the loamy soil of Estrup, ethofumesate, metamitron, and its degradation product Desamino-metamitron leached through the root zone (1 m b.g.s.) into the drainage water in average concentrations exceeding 0.1 µg/L (Table 8.1). The compounds have not been detected in deeper monitoring screens. These compounds also leached 1 m b.g.s. at the Silstrup and Faardrup sites, reaching both the drainage system (Table 8.1 and 8.2) and groundwater monitoring screens (Table 8.3 and 8.4). Average concentrations in drainage water were not as high as at Estrup, although concentrations exceeding 0.1 µg/L were observed in both drainage water and groundwater monitoring screens during a 1–6 month period at both Silstrup and Faardrup (see Kjær *et al.,* 2002 and Kjær *et al.,* 2004 for details). The above leaching was observed following an application of 345 g/ha of ethofumesate and 2,100 g/ha of metamitron in 2000 and 2003. Since then, ethofumesate has been regulated and the leaching risk related to the new admissible dose of 70 g/ha was evaluated with the two recent applications (2008 at Silstrup and 2009 at Faardrup). Although metamitron has not been regulated, a reduced dose of 1400 g/ha was applied at one of the two recent applications, namely that at Silstrup in 2008. The leaching following these recent applications (2008 at Silstrup and 2009 at Faardrup) was minor. Apart from a few samples from the drainage system and groundwater monitoring wells containing less than 0.1 µg/L, neither ethofumesate nor metamitron was found in the analysed water samples (see section 4.2.3 and 6.2.3).

- Fluazifop-P-butyl has several times been included in the monitoring programme at Jyndevad, Tylstrup, Silstrup, and Faardrup. As fluazifop-P-butyl rapidly degrades, until July 2008 monitoring has focused only on its degradation product fluazifop-P (free acid). Except for one detection below 0.1 µg/L in groundwater at Silstrup and 17 detections with eight exceeding 0.1 µg/L (four drainwater samples, three soilwater samples from the vadose zone and one groundwater sample), Table 8.2 and 8.4) at Faardrup, leaching was not evident. TFMP, the degradation product of fluazifop-P-butyl, was included in the monitoring programme at Silstrup in July 2008 following an application of fluazifop-P-butyl. After approximately one month, TFMP was detected in the groundwater monitoring wells, where concentrations at or above 0.1 µg/L were detected, within a ten-month period, following application (Figure 4.6, Table 8.3 and 8.4). At the onset of drainage flow in September, TFMP was detected in all the drainage water samples at concentrations exceeding 0.1 µg/L (Figure 4.6). The average TFMP concentration in drain water was 0.24 µg/L in 2008/09. The leaching pattern of TFMP indicates pronounced preferential flow also in periods with a relatively dry vadose zone. After use in low doses at Silstrup no leaching was observed, but in 2011/2012 after application in April 2012 TFMP was found in increasing concentrations in drain water where 0.64 µg/L was measured in June 2012. In Silstrup TFMP was found in groundwater at the end of April, and it is possible that preferential flow caused the quick leaching.

- Glyphosate and AMPA were found to leach through the root zone at high average concentrations on loamy soils. At the loamy sites Silstrup and Estrup, glyphosate has been applied two (in 2001 and 2003) and five (in 2000, 2002, 2005, 2007 and 2011) times within the monitoring period, respectively. All seven autumn applications have resulted in detectable leaching of glyphosate and AMPA from the upper meter into the drainage water, often at concentrations exceeding 0.1 µg/L several months after application. Higher leaching levels of glyphosate and AMPA have mainly been confined to the depth of the drainage system and have rarely been detected in monitoring screens located below the depth of the drainage systems, although it should be noted that detections of particularly glyphosate in groundwater monitoring wells at Estrup seem to increase over the years (Figure 5.7D). This increase may be underestimated for the period June 2007 to July 2010 as external quality assurance of analytical methods in this period indicates that the true concentration of glyphosate may be underestimated (see section 7.2.2). On two occasions heavy rain events and snowmelt triggered leaching to the groundwater monitoring wells in concentrations exceeding 0.1 µg/L more than two year after the application (Figure 5.7D). Numbers of detections exceeding 0.1 µg/L in groundwater monitoring wells are, however, very limited (only few samples). Glyphosate and AMPA were also detected in drainage water at the loamy site of Faardrup (as well as at the now discontinued Slaeggerup site), but in low concentrations (Kjær *et al.*, 2004). Evidence of glyphosate leaching was only seen on loamy soils, whereas the leaching risk was negligible on the coarse sandy soil of Jyndevad. Here, infiltrating water passed through a matrix rich in aluminium and iron, thereby providing good conditions for sorption and degradation (see Kjær *et al.*, 2005a for details).

- Two degradation products of metribuzin, diketo-metribuzin and desamino-diketo-metribuzin, leached 1 m b.g.s. at average concentrations exceeding 0.1 µg/L in the sandy soil at Tylstrup. Both degradation products appear to be relatively stable and leached for a long period of time. Average concentrations reaching 0.1 µg/L were

seen as late as three years after application (Table 8.3). Evidence was also found that their degradation products might be present in the groundwater several years after application, meaning that metribuzin and its degradation products have long-term sorption and dissipation characteristics (Rosenbom *et al.*, 2009). At both sandy sites (Tylstrup and Jyndevad), previous applications of metribuzin has caused marked groundwater contamination with its degradation products (Kjær *et al., 2005b*).

- Metalaxyl-M was applied in June 2010 and found in low concentrations in few samples from the unsaturated zone at Tylstrup. Two degradation products (CGA 62829 and CGA 108906) however, were leached from the root zone (1 m b.g.s.), and CGA 108906 in average concentrations exceeding 0.1 µg/L (Table 2.2, Figure 2.6, Table 8.1-8.4). CGA 108906 was found in 95% of the analysed groundwater samples and in 32% of the analysed samples the concentration exceeded 0.1 µg/L. Similar to the other compounds GCA 108906 was detected in samples from the upstream well of M1 and it was present in the groundwater before metalaxyl-M was applied. The background concentration makes it difficult to determine whether the elevated concentrations observed in downstream monitoring wells are due to the metalaxyl-M applied in 2010 or to previous applications "upstream". Evaluating these results it should be noted that the precipitation following the application amounted to 140 mm in July 2004 (97% higher than normal) and 111 mm in June 2004 (50% higher than normal) (see Appendix 4 and Table 2.2). During the second monitoring year CGA108906 was found more frequently and in higher concentrations at Tylstrup and Jyndevad in the unsaturated and in the saturated zone. Both degradation products were found at Jyndevad in concentrations exceeding 0.1 µg/L and in increasing concentrations.

- At Estrup, CL153815 (degradation product of picolinafen) leached through the root zone and into the drainage water in average concentrations exceeding 0.1 µg/L (Appendix 5). CL153815 has not been detected in deeper monitoring screens (Table 8.3). Leaching of CL153815 has not been observed on the sandy soil at Jyndevad after application in October 2007, (Table 8.1, Table 8.3 and Appendix 5).

- Pirimicarb together with its two degradation products pirimicarb-desmethyl and pirimicarb-desmethyl-formamido has been included in the monitoring programme for all five sites. All of the three compounds have been detected, but only pirimicarb-desmethyl-formamido leached through the root zone (1 m b.g.s.) entering the drainage system in average concentrations exceeding 0.1 µg/L (Table 8.1) at Estrup. Comparable high levels of leaching of pirimicarb-desmethyl-formamido have not been observed with any of the previous applications of pirimicarb at the other PLAP sites (Table 8.1 and Kjær *et al.*, 2004). Both degradation products (pirimicarb-desmethyl and pirimicarb-desmethyl-formamido) have been detected in deeper monitoring screens at Faardrup (Table 8.3 and 8.4).

- Propyzamide leached through the root zone (1 m b.g.s.) at the loamy Silstrup and Faardrup sites, entering the drainage system at average concentrations exceeding 0.1 µg/L (Table 8.1 and 8.2). Propyzamide was also detected in the monitoring screens situated beneath the drainage system. Apart from a few samples at Silstrup, the concentrations in the groundwater from the screens were always less than 0.1 µg/L (Appendix 5, Table 8.3 and 8.4).

- One degradation product of rimsulfuron – PPU – leached from the root zone (1 m b.g.s.) in average concentrations reaching 0.10–0.13 µg/L at the sandy soil site at Jyndevad. Minor leaching of PPU was also seen at the sandy site Tylstrup, where low concentrations (0.021-0.11 µg/L) were detected in the soil water sampled 1 and 2 m b.g.s.(Table 8.1 and 8.2). In groundwater PPU was occasionally detected and 3 samples exceeded 0.1 µg/L at Jyndevad in 2011/12, whereas it was detected in low concentration <0.1 µg/L at Tylstrup (Table 8.3 and 8.3). At both sites, PPU was relatively stable and persisted in the soil water for several years, with relatively little further degradation into PPU-desamino. E.g. average leaching concentrations reaching 0.1 µg/L were seen as much as three years after application at Jyndevad. With an overall transport time of about four years, PPU reached the downstream monitoring screens. Thus, the concentration of PPU-desamino was much lower and apart from six samples at Jyndevad, never exceeded 0.1 µg/L. It should be noted that the concentration of PPU is likely to be underestimated by up to 22-47%. Results from the field-spiked samples thus indicate that PPU is unstable and may have further degraded to PPU-desamino during analysis (Rosenbom *et al.*, 2010a).

- Terbuthylazine as well as its degradation products leached through the root zone (1 m b.g.s.) at high average concentrations on loamy soils. At the three loamy soil sites Silstrup, Estrup, and Faardrup, desethyl-terbuthylazine leached from the upper meter entering the drainage water in average concentrations exceeding 0.1 µg/L (Table 8.1 and 8.2). Four years after application in 2005 at Estrup, both terbuthylazine and desethyl-terbuthylazine were detected in drainage water, but not exceeding 0.1 µg/L. At Silstrup (Kjær *et al.*, 2007) and Faardrup (Kjær *et al.*, 2009), desethyl-terbuthylazine was frequently detected in the monitoring screens situated beneath the drainage system (Table 8.3 and 8.4), at concentrations exceeding 0.1 µg/L during a two and 24-month period, respectively. Leaching at Estrup (Kjær *et al.,* 2007) was confined to the drainage depth, however. Minor leaching of desethyl-terbuthylazine was also seen at the two sandy sites Jyndevad and Tylstrup, where desethyl-terbuthylazine was detected in low concentrations (<0.1 µg/L) in the soil water sampled 1 m b.g.s. While desethyl-terbuthylazine was not detected in the groundwater monitoring screens at Tylstrup, it was frequently detected in low concentration (< 0.1 µg/L) at Jyndevad (Table 8.4, Kjær *et al.,* 2004). Marked leaching of terbuthylazine was also seen at two of the three loamy sites (Estrup and Faardrup), the leaching pattern being similar to that of desethyl-terbuthylazine. 2-hydroxy-desethyl-terbuthylazine and hydroxy-terbuthylazine leached at both Faardrup and Estrup and at the latter site, the average drainage concentration exceeded 0.1 µg/L. Leaching of these two degradation products was at both sites confined to the drainage system. None of the two degradation products were detected in groundwater monitoring screen at Estrup, whereas at Faardrup both were found, but at low frequencies of detection and concentrations.
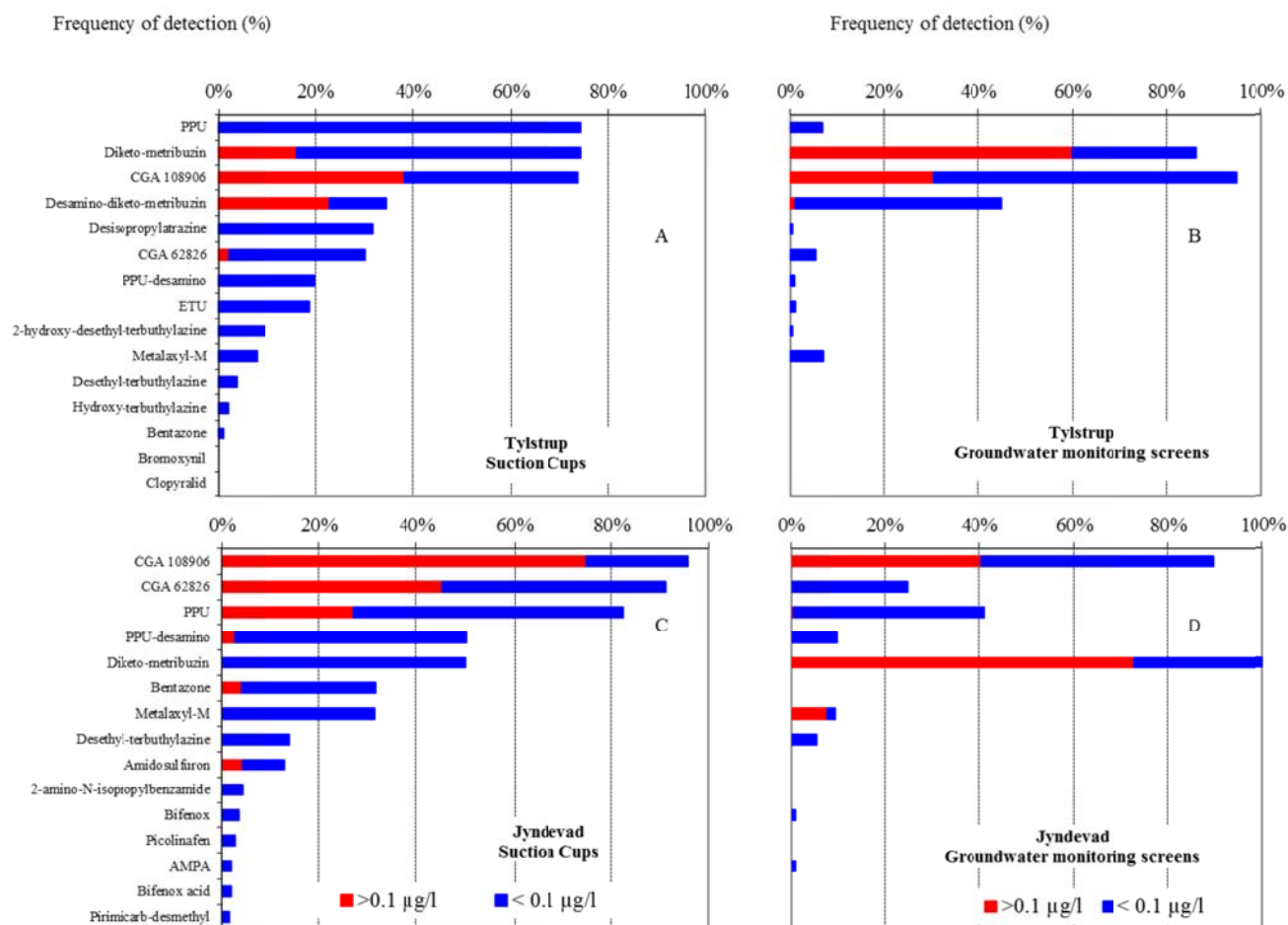
Figure 8.1. Frequency of detection in samples from the suction cups (left) and groundwater monitoring screens located deeper than the suction cups (right) at **the sandy soil sites: Tylstrup** (A, B) and **Jyndevad** (C, D). Frequency is estimated for the entire monitoring period and the length of time that the different pesticides have been included in the programme and the number of analysed samples thus varies considerably among the different pesticides. The figure only includes the fifteen most frequently detected pesticides. Pesticides monitored for less than one year are not included.

- Tebuconazole has been applied in autumn 2007 at Tylstrup, Jyndevad, Estrup and Faardrup. Only on the loamy soil of Estrup it leached through the root zone (1 m b.g.s.) and into the drainage water in average concentrations exceeding 0.1 µg/L in an average yearly concentration of 0.44 µg/L (Table 8.1 and 8.2). Leaching was mainly confined to the depth of the drainage system, although the snow melt occurring in March 2011 (more than two years after application) induced leaching of tebuconazole to the groundwater monitoring well in concentrations exceeding 0.1 µg/L (Table 8.3 and 8.4). None of the applications at the three other PLAP sites caused tebuconazole to be detected in similarly high concentrations in the vadose zone, though concentrations below 0.1 µg/L have been detected in a few samples from the groundwater monitoring screens (Table 8.3 and 8.4).
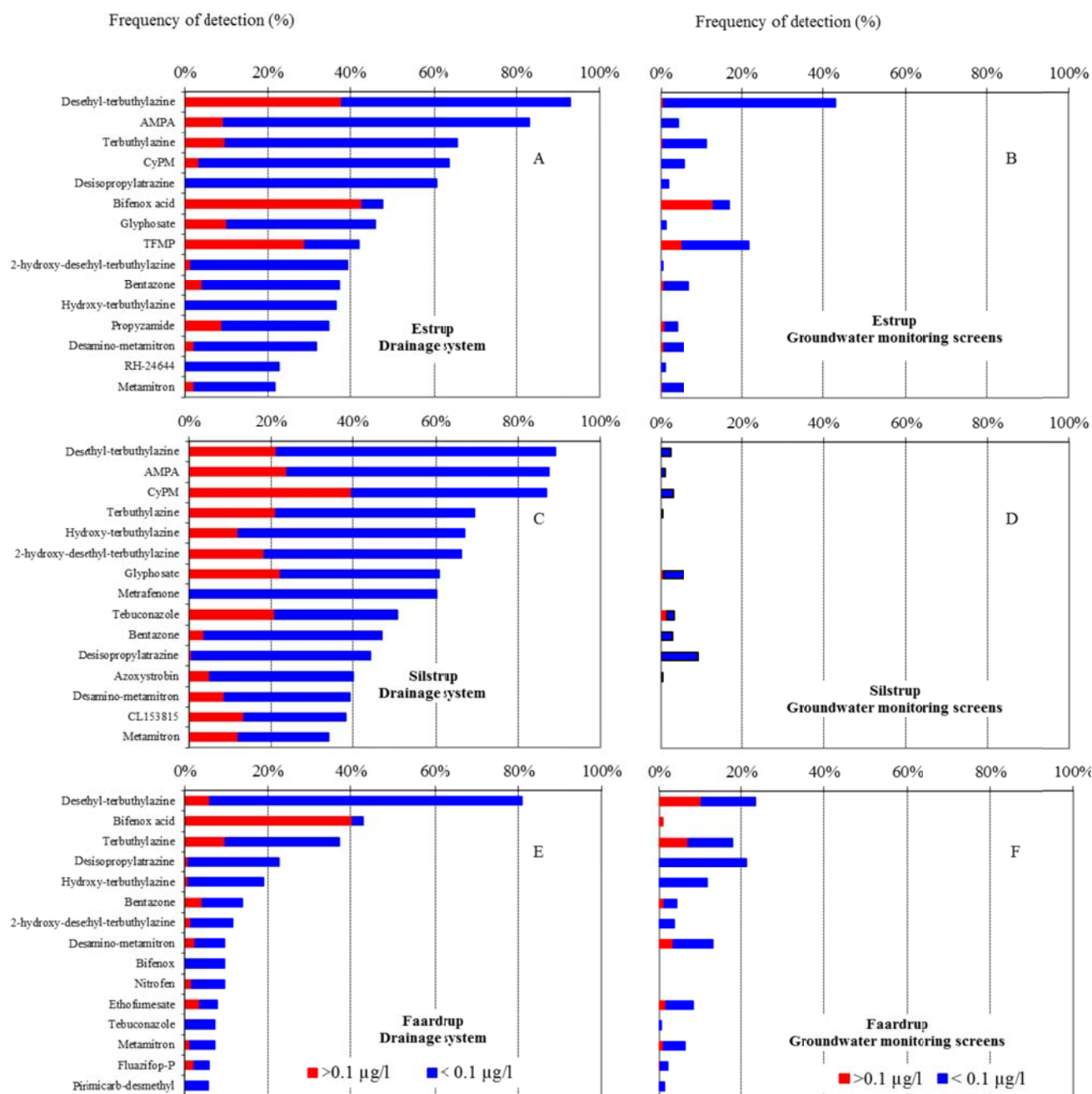
Figure 8.2. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) **at the loamy soil sites**: **Estrup** (A, B), **Silstrup** (C, D) and **Faardrup** (E, F). Frequency is estimated for the entire monitoring period and the time that the different pesticides have been included in the programme and the number of analysed samples thus varies considerably among the different pesticides. The figure only includes the fifteen most frequently detected pesticides. Pesticides monitored for less than one year are not included.

The monitoring data also indicate leaching 1 m b.g.s. of a further 18 pesticides (or their degradation products), but often in low concentrations. Although the concentrations detected 1 m b.g.s. exceeded 0.1 µg/L in several samples, the average leaching concentration (1 m b.g.s.) did not. This is summarized in Table 8.1.

Table 8.2 shows the number of samples in which the various pesticides were detected on each site as well as the maximum concentration. Apart from slight leaching of ETU (Kjær *et al.,* 2002) and amidosulfuron, within this group of 18 pesticides (or their degradation products) leaching from 1 meter was only observed at the loamy soil sites, where it was associated with pronounced macropore transport, resulting in very rapid movement of pesticides through the vadose zone. It should be noted that the findings regarding amidosulfuron are of very limited use since the degradation products – with which the leaching risk is probably mainly associated – are not included, as methods for their analysis are not yet available.

16 of the 50 pesticides applied – about 32% – did not leach at all from 1 m b.g.s. during the monitoring period (Table 8.1). The group of 16 includes the three different sulfonylureas – metsulfuron-methyl, triasulfuron, iodosulfuron-methyl-sodium and tribenuron-methyl applied at several sites. For example, tribenuron-methyl was applied at four different sites under different hydrological conditions, with percolation (1 m b.g.s.) during the first month after application ranging from 0 to 114 mm. The monitoring results give no indication of leaching for any of the compounds or their degradation products.

The leaching patterns of the sandy and loamy sites are further illustrated in Figure 8.1 and 8.2, showing the frequency of detection in samples collected 1 m b.g.s. (suction cups on sandy soils and drainage systems on loamy soils) and the deeper located groundwater monitoring screens.

On the sandy soils the number of leached pesticides as well as the frequency of detection was much lower than on loamy soils (Figure 8.1 and 8.2), the exceptions being the mobile and persistent degradation products of metalaxyl-M, rimsulfuron and metribuzin, frequently found in both suction cups and groundwater monitoring wells. This difference was mainly due to the different flow patterns characterising the two different soil types. On the sandy soils infiltrating water mainly passed through the matrix, which provide good conditions for sorption and degradation. Pesticides being leached in the sandy soils were thus restricted to mobile as well as persistent pesticides.

On the loamy soils pronounced macro pore transport resulted in the pesticides moving very rapidly through the unsaturated zone. Compared to the sandy soils residence time was much lower on the structured, loamy soils. As a result of this, various types of pesticides, even those being strongly sorbed, were prone to leaching on the loamy types of soil.

At the loamy sites pronounced leaching was generally confined to the drainage system (Figure 8.2). Several pesticides were often detected in the drainage system, whereas the frequency of detection in the monitoring screens situated beneath the drainage system was lower and varied considerably between the three sites (Figure 8.2). These differences should be seen in relation to the different sampling procedures applied. Frequent, integrated water samples can be provided from a drainage system that continuously captures water infiltrating throughout the drainage runoff season. However, although the monitoring screens situated beneath the drainage systems were sampled less frequently (on a monthly basis from a limited number of the monitoring screens (Appendix 2), pesticides were frequently found in selected screens at Faardrup and Silstrup. Hitherto, at the Estrup site, leaching of pesticides has mainly been

confined to the depth of the drainage system. Apart from 60, 91 and 58 samples containing glyphosate, desisopropyl-atrazine, and bentazone respectively, pesticides have only occasionally been detected in the screens beneath the drainage system (Appendix 5).

The differences are, however, largely attributable to the hydrological and geochemical conditions. Compared to the Silstrup and Faardrup sites, the C horizon (situated beneath the drainage depth) at the Estrup site is less permeable with less preferential flow through macro pores (see Kjær *et al.* 2005c for details). The movement of water and solute may therefore be slower at Estrup, allowing for dispersion, dilution, sorption and degradation and thereby reducing the risk of transport to deeper soil layers. An indication thereof are the long periods with groundwater table beyond drainage depth in which an increasing lateral transport to the drainage system and decreased leaching to the deeper groundwater will occur.

Comparing the loamy sites, the number of drainage water samples containing pesticides/degradation products was higher at Silstrup and Estrup than at Faardrup, which is largely attributable to the differences in the hydrological conditions.

The occurrence of precipitation and subsequent percolation within the first month after application were, generally, higher at Silstrup and Estrup than at Faardrup.

Table 8.5 are showing that a large part of the samples from the two sandy sites contain pesticides or degradation products compared with the 3 clayey sites, 43-56% and 15-40%, (one water sample can contain several substances, but the sample is only counted one time). In contrast, there has been found many pesticides and degradation products on the 3 loamy sites, also when pesticides found in concentrations >0.1 is counted.

Table 8.5. Number of water samples, water samples with findings of one or more pesticides or degradation products, and findings > 0.1 µg/L on the five PLAP sites. Number of pesticides and metabolites analysed, findings and findings >0.1 µg/L. Water samples from the period 01.01.2000–2012. Average nitrate, chloride and sulphate concentrations from groundwater, drain water and water from horizontal wells from the period 01.01.2011–01.07.2012. Avg (average).

		Fine sand Tylstrup 1	Coarse sand Jyndevad 2	Till, loam (clay) Silstrup 3	Till, loam (clay) Estrup 4	Till, loam (clay) Faardrup 5	All sites
Water samples	Number analysed	1.725	1.701	2.139	3.181	2.156	10.902
	With findings	970	733	744	1.274	327	4.048
	Findings >0.1 µg/L	469	210	193	682	91	1.645
	Findings %	56	43	35	40	15	37
	>0.1 µg/L	27	12	9	21	4	15
Pesticides and metabolites	Number analysed	57	58	66	58	57	101*
	With findings	16	19	39	45	38	76
	Findings >0.1 µg/L	6	9	22	31	21	56
	Findings %	28.1	32.8	59.1	77.6	66.7	75.2
	>0.1 µg/L	10.5	15.5	33.3	53.4	36.8	55.4
Groundwater	Nitrate-N avg	15.5	11.9	3.0	0.4	8.5	
	Chloride avg	49.9	15.6	29.5	11.7	27.1	
	Sulphate-S avg	15.3	10.0	7.6	7.5	8.3	
Drainwater	Nitrate-N avg			2.1	3.5	11.2	
	Chloride avg			30.3	26.6	27.5	
	Sulphate-S avg			6.5	4.9	10.5	
Horizontal well	Nitrate-N avg	8.4	4.1	2.6	0.3	11.3	
	Chloride avg	94.8	29.0	31.1	30.3	30.0	
	Sulphate-S avg	27.0	10.0	8.2	10.9	10.7	

*Diflufenican applied after April 2012, but included in this table.

On the 3 loamy sites 59-78% of the applied pesticides were found in drain or groundwater after application, while 28-32% was found in water samples from the sandy sites.

The nitrate concentrations are very high under the sandy soils, and therefore the findings of pesticides in many samples from the two sandy soils presumable are due to a combination of use of persistent pesticides on sandy soil, while quick transport through macro pores may cause findings of many different pesticides in clay/loamy soils.

The nitrate content is very high on Faardrup, where there is a low finding of pesticides. The leaching of pesticides and degradation products is probably caused by a combination of pesticide selection, hydraulic conditions, type of agriculture and leaching of nutrients.

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Appendixes

Appendix 1
Chemical abstracts nomenclature for the pesticides encompassed by the PLAP

Appendix 2
Pesticide monitoring programme – Sampling procedure

Appendix 3
Agricultural management

Appendix 4
Precipitation data for the PLAP sites

Appendix 5
Pesticide detections in samples for drains, suction cups and groundwater monitoring wells

Appendix 6
Laboratory internal control cards

Appendix 7
Pesticides analysed at 5 PLAP sites in the period up to 2007

Appendix 8
New horizontal wells

Appendix 1

Chemical abstracts nomenclature for the pesticides encompassed by the PLAP

Table A1.1. Systematic chemical nomenclature for the pesticides and degradation products encompassed by the PLAP. P (parent). M (metabolite).

Parent pesticide	P/M	Analyte	Systematic name
Aclonifen	P	Aclonifen	2-chloro-6-nitro-3-phenoxyaniline
Amidosulfuron	P	Amidosulfuron	N-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-N-methylmethanesulfonamide
Amidosulfuron	M	Desmethyl-amidosulfuron	3-(4-hydroxy-6-methoxypyrimidin-2-yl)-1-(N-methyl-N-methylsulfonyl-aminosulfonyl)-urea
Aminopyralid	P	Aminopyralid	4-amino-3,6-dichloropyridine-2-carboxylic acid
Azoxystrobin	P	Azoxystrobin	Methyl (E)-2-{2-[(6-(2-cyanophenoxy)-4-pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate
Azoxystrobin	M	CyPM	E-2-(2-[6-cyanophenoxy)-pyrimidin-4-yloxy]-phenyl) – 3-methoxyacrylic acid
Bentazone	M	2-amino-N-isopropylbenzamid	2-amino-N-isopropylbenzamide
Bentazone	P	Bentazone	3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2 dioxide
Bifenox	P	Bifenox	methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate
Bifenox	M	Bifenox acid	5-(2,4-dichlorophenoxy)-2-nitrobenzoic acid
Bifenox	M	Nitrofen	2,4-dichlorophenyl 4'-nitrophenyl ether
Boscalid	P	Boscalid	2-chloro-N-(4'-chlorobiphenyl-2-yl)nicotinamide
Bromoxynil	P	Bromoxynil	3,5-dibromo-4-hydroxybenzonitrile
Chlormequat	P	Chlormequat	2-chloroethyltrimethylammonium chloride
Clomazon	P	Clomazon	2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidione
Clomazon	M	FMC65317	(N-[2- chlorophenol)methyl] -3-hydroxy-2,2- dimethyl propanamide (Propanamide-clomazone)
Clopyralid	P	Clopyralid	3,6-Dichloropyridine-2-carboxylic acid
Cyazofamid	P	Cyazofamid	4-chloro-2-cyano-N,N-dimethyl-5-p-tolylimidazole-1-sulfonamide
Desmedipham	P	Desmedipham	Ethyl 3-(phenylcarbamoyloxy)phenylcarbamate
Desmedipham	M	EHPC	Carbamic acid, (3-hydroxyphenyl)-ethyl ester
Diflufenican	M	AE-05422291	2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxamide
Diflufenican	M	AE-B107137	2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxylic acid
Diflufenican	P	Diflufenican	2',4'-difluoro-2-(a,a,a-trifluoro-m-tolyloxy)nicotinanilide
Dimethoat	P	Dimethoat	O,O-dimethyl S-methylcarbamoylmethyl-phosphorodithioate
Epoxiconazole	P	Epoxiconazole	(2RS, 3SR)-1-(2-(2-chlorophenyl)-2,3-epoxy-2-(4-fluorophenyl)propyl)-1H-1,2,4-triazol
Ethofumesat	P	Ethofumesat	(±)-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl-methanesulfonate
Fenpropimorph	P	Fenpropimorph	Cis-4-[3-[4-(1,1-dimethylethyl)-phenyl]-2-methylpropyl]-2,6-imethylmorpholine
Fenpropimorph	M	Fenpropimorph-acid	Cis-4-[3-[4-(2-carboxypropyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine
Flamprop-M-isopropyl	M	Flamprop (free acid)	N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alanine
Flamprop-M-isopropyl	P	Flamprop-M-isopropyl	Isopropyl N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alaninate
Florasulam	P	Florasulam	2',6',8-Trifluoro-5-methoxy-s-triazolo [1,5-c]pyrimidine-2-sulfonanilide
Florasulam	M	Florasulam-desmethyl	N-(2,6-difluorophenyl)-8-fluro-5-hydroxy[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide
Fluazifop-P-buthyl	M	Fluazifop-P (free acid)	(R)-2-(4-((5-(trifluoromethyl)-2-pyridinyl)oxy)phenoxy-propanoic acid
Fluazifop-P-buthyl	P	Fluazifop-P-buthyl	butyl (R)-2-{4-[5-(trifluoromethyl)-2-pyridyloxy]phenoxy}propionate
Fluazifop-P-buthyl	M	TFMP	5-trifluoromethyl-pyridin-2-ol
Fluroxypyr	P	Fluroxypyr	(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid
Glyphosate	M	AMPA	Amino-methylphosphonic acid
Glyphosate	P	Glyphosate	N-(phosphonomethyl)glycine
Iodosulfuron-methyl-natrium	P	Iodosulfuron-methyl-natrium	sodium salt of methyl 4-iodo-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate
Iodosulfuron-methyl-natrium	P	Metsulfuron methyl	methyl 2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)benzoate
Ioxynil	P	Ioxynil	4-hydroxy-3,5-diiodobenzonitrile
Isoproturon	P	Isoproturon	N,N-dimethyl-N'-[4-(1-methylethyl)phenyl]urea
Linuron	P	Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
Mancozeb	M	ETU	Ethylenethiourea
MCPA	M	4-chlor-2-methylphenol	2-methyl-4-chlorophenol
MCPA	P	MCPA	(4-chloro-2-methylphenoxy)acetic acid
Mesosulfuron-methyl	M	Mesosulfuron	2-[[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-4-[[(methylsulfonyl)amino]methyl]benzoic acid

Table A1.1 continued. Systematic chemical nomenclature for the pesticides and degradation products encompassed by the PLAP. P (parent). M (metabolite).

Parent pesticide	P/M	Analyte	Systematic name
Mesosulfuron-methyl	P	Mesosulfuron-methyl	Methyl 2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-4-methanesulfonamidomethylbenzoate
Mesotrione	M	AMBA	2-amino-4-methylsulfonylbenzoic acid
Mesotrione	P	Mesotrione	2-(4-mesyl-2-nitrobenzoyl)cyclohexane-1,3-dione
Mesotrione	M	MNBA	methylsulfonyl-2-nitrobenzoic acid
Metalaxyl-M	M	CGA 108906	2-[(1-carboxyethyl)(methoxyacetyl)amino]-3-methylbenzoic acid
Metalaxyl-M	M	CGA 62826	2-[(2,6-dimethylphenyl)(methoxyacetyl)amino]propanoic acid
Metalaxyl-M	P	Metalaxyl-M	methyl N-(methoxyacetyl)-N-(2,6-xylyl)-D-alaninate
Metamitron	P	Metamitron	4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one
Metamitron	M	Metamitron-desamino	4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazine-5-one
Metrafenone	P	Metrafenone	3'-bromo-2,3,4,6'-tetramethoxy-2',6-dimethylbenzophenone
Metribuzin	P	Metribuzin	4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-5-one
Metribuzin	M	Metribuzin-desamino	6-(1,1-dimethylethyl)-3-(methylthio)- 1,2,4-triazin-5-(4H)-one
Metribuzin	M	Metribuzin-desamino-diketo	6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-3,5-dione
Metribuzin	M	Metribuzin-diketo	4-amino-6-tert-butyl-4,5-dihydro-1,2,4-triazine-3,5-dione
Pendimethalin	P	Pendimethalin	N-(1-ethyl)-2,6-dinitro-3,4-xynile
Phenmedipham	M	3-aminophenol	1-amino-3-hydroxybenzene
Phenmedipham	M	MHPC	Methyl-N-(3-hydoxyphenyl)-carbamate
Phenmedipham	P	Phenmedipham	3-[(methoxycarbonyl)amino]phenyl (3-methylphenyl)carbamate
Picolinafen	M	CL153815	6-(3-trifluoromethylphenoxy)-2-pyridine carboxylic acid
Picolinafen	P	Picolinafen	4'-fluoro-6-(a,a,a-trifluoro-m-tolyloxy)pyridine-2-carboxanilide
Pirimicarb	P	Pirimicarb	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyldimethylcarbamate
Pirimicarb	M	Pirimicarb-desmethyl	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate
Pirimicarb	M	Pirimicarb-desmethyl-formamido	2-methylformamido-5,6-dimethylpyrimidine-4-yl dimethylcarbamate
Propiconazol	P	Propiconazol	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole
Propyzamid	P	Propyzamid	3,5-dichloro-N-(1,1-dimethylprop-2-ynyl)benzamide
Propyzamid	M	RH24580	N-(1,1-dimethylacetonyl)-3,5-dichlorobenzamide
Propyzamid	M	RH24644	2-(3,5-dichlorophenyl)-4,4-dimethyl-5-methylene-oxalzoline
Propyzamid	M	RH24655	3,5-dichlor-N-(1,1-dimethylpropenyl)benzamide
Prosulfocarb	P	Prosulfocarb	N-[[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-[2-(3,3,3,-triflu=propyl)phenylsulfonyl]urea
Pyridat	M	PHCP	3-phenyl-4-hydroxy-6-chloropyridazine
Pyridat	P	Pyridat	O-6-chloro-3-phenylpyridazin-4-yl S-octyl thiocarbonate
Rimsulfuron	M	IN70941	N-(4,6-dimethoxy-2-pyrimidinyl-N-((3-ethylsulfonyl)-2-pyridinyl)urea (IN70941)
Rimsulfuron	M	IN70942	N-((3-(ethylsulfonyl)-2-pyridyl)-4,6 dimethoxy-2 pyrimidinamine (IN70942)
Rimsulfuron	P	Rimsulfuron	N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide
Tebuconazole	P	Tebuconazole	a-[2-(4-chlorophenyl)ethyl]-a-(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol
Terbuthylazin	M	2-hydroxy-desethyl-terbuthylazine	6-hydroxy-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine
Terbuthylazin	M	2-hydroxy-terbuthylazin	6-hydroxy-N-(1,1-dimethylethyl)-N´-ethyl-1,3,5,triazine-2,4-diamine
Terbuthylazin	M	Desethylterbuthylazin	6-chloro-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine
Terbuthylazin	M	Desisopropylatrazin	6-chloro-N-ethyl-1,3,5-triazine-2,4-diamine
Terbuthylazin	P	Terbuthylazin	6-chloro-N-(1,1-dimethylethyl)-N-ethyl-1,3,5-triazine-2,4-diamine
Thiacloprid	M	M2	(3-[(6-chloro-3-pyridinyl)methyl]-2-thiazolidinylidene) urea
Thiacloprid	M	M30	sodium 2-[[[(aminocarbonyl)amino]-carbonyl][(6-chloro-3-pyridinyl)-methyl]amino]ethanesulfonate
Thiacloprid	M	M34	2-{carbamoyl[(6-chloropyridin-3-yl)methyl]amino}etanesulfonic acid
Thiacloprid	P	Thiacloprid	(Z)-3-(6-chloro-3-pyridylmethyl)-1,3-thiazolidin-2-ylidenecyanamide
Thiamethoxam	M	CGA 322704	[C(E)]-N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N'-nitroguanidine
Thiamethoxam	P	Thiamethoxam	3-(2-cholro-thiazol-5-ylmethyl)-5-methyl[1,3,5]oxadiazinan-4ylidene-N-nitroamine
Triasulfuron	P	Triasulfuron	1-[2-(2-chloroethoxy)phenylsulfonyl]-2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl)-urea
Triasulfuron	M	Triazinamin	2-amino-4-methoxy-6-methyl-1,3,5-triazine
Tribenuron-methyl	M	Triazinamin-methyl	4-methoxy-6-methyl-1,3,5-triazin-methylamine
Tribenuron-methyl	P	Tribenuron-methyl	methyl 2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoylsulfamoyl]benzoate
Triflusulfuron-methyl	M	IN-D8526	N,N-dimethyl-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine
Triflusulfuron-methyl	M	IN-E7710	N-methyl-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine
Triflusulfuron-methyl	M	IN-M7222	6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine
Triflusulfuron-methyl	P	Triflusulfuron-methyl	methyl 2-[4-dimethylamino-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-ylcarbamoylsulfamoyl]-m-toluate

Appendix 2

Pesticide monitoring programme – Sampling procedure

From each of the PLAP sites, samples were collected of groundwater, drainage water and soil water in the unsaturated zone. A full description of the monitoring design and sampling procedure is provided in Lindhardt *et al*. (2001) and Kjær *et al*. (2003), respectively.

Until March 2002, pesticide analysis was performed monthly on water samples from the suction cups located both 1 m b.g.s. and 2 m b.g.s., from two screens of the horizontal monitoring wells and from two of the downstream vertical monitoring wells. In addition, more intensive monitoring encompassing all four groups of suction cups, six screens of the horizontal monitoring wells and five monitoring wells was performed every four months (Kjær *et al.*, 2002). At the loamy sites, the pesticide analysis was also performed on drainage water samples.

The monitoring programme was revised in March 2002 and the number of pesticide analyses was reduced. At the loamy sites, pesticide analysis of water sampled from the suction cups was ceased, and the monthly monitoring was restricted to just one monitoring well. At Jyndevad, pesticide analysis of the suction cups located 2 m b.g.s. was ceased and the interval for the intensive monitoring encompassing the larger number of monitoring screens was extended to six months, except for the suction cups 2 m b.g.s. at Tylstrup, where the four-month interval was retained (Kjær *et al.*, 2003).

On the sandy soils, the analysis of a number of pesticides in water from the monitoring wells had to be further reduced, due to economical constraints imposed by the high prices on pesticide analysis. This reduction was based on results from the suction cups implying that leaching risk of certain pesticides was negligible, why analysis of a limited number of groundwater samples would be reasonable (see Table A5.1 and Table A5.2 in Appendix 5).

Table A2.1. Pesticide monitoring programme in suction cups (S), horizontal monitoring wells (H) and vertical monitoring wells (M) as of March 2009. Water sampling places (S, H, and M) from where sampling stopped in 2008 and 2009 are given in bold. Well M10 at Silstrup was included in the programme on 5 February 2009.

Site	Monthly monitoring (Intensive)	Half-yearly monitoring (Extensive)	Not monitored
Tylstrup	M4, M5, S1a, S2a	M1, M3, M4, M5, S1a, S2a, S1b*, S2b*	M2, **M6**, M7
Jyndevad	M1, M4, S1a, S2a	M1, M2, M4, M5, M7, S1a, S2a	M3, **M6**, S1b, S2b
Silstrup	M5, H1.2	M5, M9, M10. M12, H1.1, H1.2, H1.3	M1, M2**, M4,M6**, M8, M7,M11, **M13**, **H2.1**, **H2.2**, **H2.3**
Estrup	M4, H1.2	M1, M4, M5, M6, H1.1, H1.2, H1.3	M2, **M3**, **M7,**
Faardrup	M4, M5, H2.3	M4, M5, M6, H2.1, H2.3, H2.5	M1, **M2**, **M3**, **M7, H1.1**, H1.2, **H1.3**

S1a and S1b refer to suction cups installed 1 and 2 m b.g.s., respectively, at location S1, whereas S2a and S2b refer to suction cups installed 1 and 2 m b.g.s., respectively, at location S2.
At Tylstrup suctions cups installed 2 m b.g.s.are monitored four times a year (see text).

In March 2008, a new revision of the monitoring programme was completed resulting in an optimization of the programme including an additional reduction in the sampling programme (Table A2.1). On the loamy sites, sampling from the suction cups for inorganic analysis, from one-two monitoring wells per site, and one horizontal well at Silstrup (H2) and Faardrup (H1) was suspended. On the sandy sites, only sampling from the monitoring well M6 at Tylstrup has been suspended (see Rosenbom *et al.,* 2010b for details).

Until July 2004, pesticide analyses were performed weekly on water sampled time-proportionally from the drainage system. Moreover, during storm events additional samples (sampled flow-proportionally over 1–2 days) were also analysed for pesticides. In June 2004 the drainage monitoring programme was revised. From July 2004 and onwards pesticide analyses were done weekly on water sampled flow- proportionally from the drainage water system. See Kjær *et al.* 2003 for further details on the methods of flow-proportional sampling. The weighted average concentration of pesticides in the drainage water was calculated according to the following equation:

$$C = \frac{\sum_{i=1}^{n} M_i}{\sum_{i=1}^{n} V_i}$$

$$M_i = C_i \cdot V_i$$

where:
n =   Number of weeks within the period of continuous drainage runoff
V_i=   Weekly accumulated drainage runoff (mm/week)
C_i=   Pesticide concentration collected by means of the flow-proportional sampler (μg/L)

Until July 2004 where both time and flow-proportional sampling was applied the numbers were:
$M_i = Ct_i \cdot V_i$ *If no flow event occurs within the i'th week*
$M_i = Cf_i \cdot Vf_i$ *If a flow event occurs within the i'th week and if $Cf_i \cdot Vf_i > Ct_i \cdot V_i$*

where:
n =   Number of weeks within the period of continuous drainage runoff
V_i=   Weekly accumulated drainage runoff (mm/week)
Vf_i =   Drainage runoff accumulated during a "flow event" (mm/storm event)
Cf_i=   Pesticide concentration in the "event samples" collected by means of the flow-proportional sampler (μg/L)
Ct_i=   Pesticide concentration in the weekly samples collected by means of the time-proportional sampler (μg/L)

Table 2.2, 3.2, 4.2, 5.2 and 6.2 report the weighted average leachate concentration in the drainage water within the first drainage season after application. In these tables this calculation period is defined as the period from application until 1 July the following year, as pesticides are usually present in the first drainage runoff occurring after application of pesticide.

On the sandy soils the weighted average concentration of pesticides leached to the suction cups situated 1 m b.g.s. was estimated using the measured pesticide concentration and estimated percolation on a monthly basis. Pesticide concentrations measured in suction cups S1 and S2 were assumed to be representative for each sample period. Moreover, accumulated percolation rates deriving from the MACRO model were assumed to be representative for both suction cups S1 and S2. For each of the measured concentrations, the corresponding percolation (Perc.) was estimated according to the equation:

$$P_i = \sum\nolimits_{t_1}^{t_2} P_t$$

where:
t =   sampling date; $t_1 = 0.5(t_{i-1}+t_i)$; $t_2 = 0.5(t_i+t_{i+1})$
P_t =   daily percolation at 1 m b.g.s. as estimated by the MACRO model (mm)

The average concentration was estimated according to the equation:

$$C = \frac{\sum C_i \cdot P_i}{\sum P_i}$$

where:
C_i =   measured pesticide concentration in the suction cups located 1 m b.g.s.

Table 2.2 and 3.2 report the weighted average leachate concentration. In these tables this calculation period is defined as the period from the date of first detection until 1 July the following year. On sandy soils the transport of pesticides down to the suction cups situated at 1 m depth may take some time. In most cases the first detection of pesticides occurs around 1 July, why the reported concentration represents the yearly average concentration. In a few cases the first detection of pesticides occurs later, but this later occurrence does not affect the weighted average calculation. E.g. the reported average concentration using a calculation period from the first detection until 1 July the following year is equal to that using a calculation period of a year (1 July–30 June) the following year). Unless noted the concentrations listed in Table 2.2 and 3.2 can therefore be considered as yearly average concentrations. In the few cases where reported concentrations are either not representative for an annual average concentration or not representative for the given leaching pattern (leaching increases the second or third year after application) a note is inserted in the table.

Appendix 3

Agricultural management

Table A3.1. Management practice at **Tylstrup** during the 2007 to 2011 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
01/08/2007	Direct harwest and simultaniusly shreeding the straw. Seed yield 24.5 hkg/ha 91% DM. Straw amount 64,7 hkg/ha 100% DM incl. stubble
03/08/2007	Rotary cultivated - depth 3.0 cm (straw incorporation)
07/09/2007	Rotary cultivated - depth 7.0 cm (straw incorporation)
12/09/2007	Ploughed - depth 22 cm
12/09/2007	Rolled with concrete roller
24/09/2007	Sowing winter wheat, cv. Smuggler. sowing depth 3.9 cm, seeding rate 172 kg/ha , row distance 13 cm, final plantnumber 264/m^2
18/10/2007	Stomp (pendimethalin) - weeds - 5.0 l/ha
16/11/2007	Folicur EC250 (tebuconazol) - fungi - 1.0 l/ha
22/05/2008	Irrigation 32 mm Started 22/5 23.00 Ended 23/5 07.00
29/05/2008	Irrigation 32 mm Started 29/5 23.00 Ended 30/5 07.00
05/06/2008	Irrigation 30 mm Started 05/06 22.00 Ended 06/06 07.00
13/06/2008	Irrigation 30 mm Started 13/06 22.00 Ended 14/06 07.00
17/06/2008	Amistar (azoxystrobin) - fungi - 1.0 l/ha
18/08/2008	Harvest of winter wheat. Stubleheight 17 cm, grainyield 92.1 hkg/ha 85% DM
31/08/2008	Strawyield amount 18.5 hkg/ha 100% DM
19/09/2008	Stubbleharrowed across twice - depth 5.0 cm
14/10/2008	Stubbleharrowed - depth 7.0 cm
10/04/2009	Ploughed - depth 24 cm
10/04/2009	Rolled with concrete roller
14/04/2009	Spring barley sown, cv. Keops, seeding rate 170 kg/ha, sowing depth 2.5 cm, row distance 13 cm. Using combine driller with a tubular packer roller, Finalplant number 392 /m^2
15/05/2009	Basagran M75 (bentazone+MCPA) - weeds - 1.5 l/ha
23/06/2009	Amistar (azoxystrobin) - fungi - 1.0 l/ha
29/06/2009	Irrigation 26 mm. Started 29/06 23.00 Ended 30/07 07.00
08/07/2009	Irrigation 27 mm. Started 08/07 23.00 Ended 09/07 07.00
08/07/2009	Mavrik 2F (tau-fluvalinate) - pests - 0.1 l/ha (not analyzed)
20/08/2009	Harvest of spring barley. Stubleheight 16 cm, grainyield 53.4 hkg/ha 85% DM
28/08/2009	Straw removed, yield 17.4 hkg/ha 100% DM
04/04/2010	Ploughed - depth 24 cm
26/04/2010	Rolled with concrete roller
04/05/2010	Seed bed preparation, 10.0 cm depth (across)
06/05/2010	Planting of potatoes. cv. Kuras rowdistance 75 cm, plantdistance 25 cm, depth 17 cm, final plantnumber 4,0/m^2
17/05/2010	Ridging
26/05/2010	Fenix (aclonifen) - weeds - 1.0 l/ha + Titus WSB (rimsulfuron) - weeds - 10 g/ha
08/06/2010	Titus WSB (rimsulfuron) - weeds - 20 g/ha
15/06/2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
24/06/2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
01/07/2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
06/07/2010	Irrigation 29 mm. Started 06/07 22:00 Ended 07/07 07:00
09/07/2010	Ridomil Gold MZ Pepite (mancozeb - metalaxyl) - fungi - 2.0 kg/ha
16/07/2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
23/07/2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
27/07/2010	Irrigation 28 mm. Started 27/07 22:00 Ended 28/07 07:00
02/08/2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
09/08/2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha
17/08/2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha
23/08/2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha
20/10/2010	Harvest of potatoes. Tuber yield 128,02 hkg/ha - 100% DM
17/04/2011	Ploughed - depth 24 cm.
18/04/2011	Rolled with concrete roller
19/04/2011	Spring barley sown, cv.TamTam, seeding rate 180 kg/ha, sowing depth 3.3 cm, row distance 12.5 cm. Final plantnumber 365 /m2

Date	Management practice
19/04/2011	Seed bed preparation, 8 cm depth
10/05/2011	Oxitril CM (ioxynil + bromoxynil) - weeds - 0.4 l/ha (not analyzed)
20/06/2011	Bell (boscalid + epoxiconazole) - fungi - 1.5 L/ha

Table A3.2. Management practice at **Jyndevad** during the 2007 to 2011 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
07/08/2007	Harvest of triticale. Seed yield 38.7 kgh/ha 85% DM, strawyield 38.3 hkg/ha 100% DM, stubbleheight 15 cm
13/09/2007	Roundup (glyphosate) - weeds - 2.0 l/ha
28/09/2007	Ploughed. Depth 22 cm
29/09/2007	Rolled with a concrete roller
01/10/2007	Sowing winter wheat cv. Ambition. Depth 4.5 cm, seeding rate 175 kg/ha, row distance 12 cm using rotorharrow/combine drill, Final plantnumber 291 m^2
30/10/2007	Pico 750 WG (picolinafen) - weeds - 0.133 g/ha
03/12/2007	Folicur EC 250 (tebuconazole) - fungi - 1.0 L/ha
07/05/2008	Irrigation - 42 mm/ha
14/05/2008	Irrigation - 27 mm/ha
21/05/2008	Irrigation - 27 mm/ha
30/05/2008	Irrigation - 30 mm/ha
05/06/2008	Irrigation - 35 mm/ha
11/06/2008	Amistar (azoxystrobin) - fungi - 1.0 l/ha
25/06/2008	Irrigation - 35 mm/ha
08/07/2008	Irrigation - 30 mm/ha
30/08/2008	Harvest of winter wheat. Stubleheight 15 cm, grainyield 68,1 hkg/ha 85% DM, strawyield 28,1 hkg/ha 100% DM
17/03/2009	Ploughed. Depth 22 cm
18/03/2009	Sowing spring barley cv. Simba, depth 4,0 cm, rowdistance 12 cm, seed rate 200 kg/ha, final plantnumber 320 m^2 - using a combine drill.
18/03/2009	Rolled with a concrete roller
27/04/2009	Fox 480 SC (bifenox) - weeds - 1.2 l/ha
11/05/2009	Basagran M75 (bentazone+MCPA) - weeds - 1.5 l/ha
26/05/2009	Bell (boscalid + epoxiconazole) - fungi - 1.5 l/ha
27/05/2009	Irrigation - 30 mm/ha started on 27/5 ended on 28/5
05/06/2009	Irrigation - 27 mm/ha started on 5/5 ended on 6/5
29/06/2009	Irrigation - 27 mm/ha started on 29/6 ended on 30/6
07/08/2009	Harvest of spring barley. Seed yield 63.96 hkg/ha 85% DM, strawyield 19.5 hkg/ha 100% DM, stubbleheight 15 cm
14/04/2010	Ploughed. Depth 24 cm
15/04/2010	Rolled with concrete roller
22/04/2010	Seed bed preparation. 9.0 cm depth
04/05/2010	Planting of potatoes. cv. Kuras rowdistance 75 cm, plantdistance 33 cm, depth 8 cm, final plantnumber 4,0/m^2
04/05/2010	Ridging
27/05/2010	Fenix (aclonifen) - weeds - 1.0 l/ha + Titus WSB (rimsulfuron) - weeds - 10 g/ha
08/06/2010	Titus WSB (rimsulfuron) - weeds - 20 g/ha
24/06/2010	Irrigation - 25 mm/ha started on 24/6 ended on 25/6
28/06/2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
30/06/2010	Irrigation - 25 mm/ha started on 30/6 ended on 1/7
06/07/2010	Amistar (azoxystrobin) - fungi - 0.5 l/ha
07/07/2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
08/07/2010	Irrigation - 30 mm/ha started on 8/7 ended on 9/7
14/07/2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
16/07/2010	Karate 2,5 WG (Lambda-cyhalothrin) - 0.3 kg/ha (not analyzed)
25/07/2010	Ridomil Gold MZ Pepite (mancozeb - metalaxyl-M) - fungi - 2.0 kg/ha
01/08/2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
09/08/2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
16/08/2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
23/08/2010	Tyfon (propamocarb+fenamidone) - fungi - 2 l/ha (not analyzed)
31/08/2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha (not analyzed)
10/09/2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha (not analyzed)
23/09/2010	Shirlan (fluazinam) - fungi - 0.4 l/ha (not analyzed)
19/10/2010	Harvest of potatoes Yield in tubers 120.6 hkg/ha, 100% DM
22/03/2011	Ploughed. Depth 24 cm
23/03/2011	Sowing spring barley cv. Quench, depth 4.0 cm, rowdistance 12 cm, seed rate 164 kg/ha, final plantnumber 301 m^2 - using a combine drill
24/03/2011	Rolled with concrete roller
26/04/2011	Oxitril CM (bromoxynil + ioxynil) - 0.5 l/ha (not analyzed) + DFF (diflufenican) - 0.25 l/ha- weeds
02/05/2011	Irrigation - 30 mm/ha started on 02/05 ended on 03/05
23/05/2011	Irrigation - 32 mm/ha started on 23/05 ended on 24/05

Table A3.3. Management practice at **Silstrup** during the 2007 to 2011 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
24/08/2007	Harvest of winter wheat. Grain yield 100.7 hkg/ha 85% DM, strawyield 40.8 hkg/ha 100% DM, stubbleheight 0 cm (incorprated)
24/08/2007	Straw shredded. Amount 100.9 hkg/ha incl stubble
29/08/2007	Stubble harrowed, heavy disk harrow (Dalbo) - depth 5 cm
12/11/2007	Ploughed - depth 27 cm
21/04/2008	Harrowed - depth 5 cm and packed
22/04/2008	Levelled and rolled with Cambridge roller
05/05/2008	Harrowed accross - depth 10 cm
07/05/2008	Sowing fodder beet cultivare Kyros. depth 1.3 cm rowdistance 62.5 cm plantdistance 18-20 cm. seeding rate 2.5 kg/ha. Final plantnumber 5.5/m^2
22/05/2008	30 g/ha Safari (triflusulfuron-methyl) + 0.5 L/ha Goliath (metamitron) + 1.5 L/ha Betanal (phenmedipham) – weeds
30/05/2008	30 g/ha Safari (triflusulfuron-methyl) + 0.5 L/ha Goliath (metamitron) + 1.5 L/ha Betanal (phenmedipham) + 0.07 L/haTramat 500 SC (ethofumesate) –weeds
17/06/2008	30 g/ha Safari (triflusulfuron-methyl) + 0.5 L/ha Goliath (metamitron) + 1.5 L/ha Betanal (phenmedipham) + 0.07 L/haTramat 500 SC (ethofumesate) –weeds
26/06/2008	Pirimor G (pirimicarb) - pests - 0.300 kg/ha
01/07/2008	Fusilade Max (fluazifop-P-butyl) - weeds - 3.0 l/ha
04/07/2008	30 g/ha Safari (triflusulfuron-methyl) + 0.5 L/ha Goliath (metamitron) + 1.5 L/ha Betanal (phenmedipham) – weeds
09/07/2008	Pirimor G (pirimicarb) - pests - 0.300 kg/ha
27/10/2008	Harvest of fodder beet. Yield of root 17.25 t/ha 100% DM, yield of top 5.15 t/ha 100% DM.
15/12/2008	Ploughed - depth 23 cm
30/03/2009	Harrowed 2 times across - depth 5 cm
02/04/2009	Tracer (potasium bromide). 31.5 kg/ha
11/04/2009	Sowing spring barley cv. Keops depth 3.5 cm, row distance 15 cm, seeding rate 120 kg/ha, final plantnumber 263/m^2. Undersown red fescue cv. Jasperina, broadcast, seeding rate 8.8 kg/ha
11/04/2009	Rolled with Cambridge roller
19/05/2009	Fighter 480 (bentazone) - weeds - 1.25 l/ha
24/06/2009	Amistar (azoxystrobin) - fungi - 1.0 l/ha
16/07/2009	Whole crop harvest, 94.6 hkg/ha 100% DM stubble height 15 cm
24/08/2009	Hussar OD (iodosulfuron-methyl) - weeds - 0.020 l/ha
09/09/2009	Fox 480 SC (bifenox) - weeds - 1.5 l/ha
02/05/2010	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 l/ha
05/05/2010	Hussar OD (iodosulfuron) + SweDane MCPA 750 - weeds - 0.1 l/ha + 0.7 l/ha
20/07/2010	Harvest of grass seed. Yield 16.5 hkg/ha 87% DM, stubble height 12 cm,
21/07/2010	Straw burned, 69.3 hkg/ha 100% DM
21/07/2010	Harvest of grass seed. Yield 15.2 hkg/ha 87% DM, stubble height 5 cm.
15/04/2011	Hussar OD (iodosulfuron) - weeds - 0.05 l/ha (not analyzed)
26/04/2011	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 l/ha

Table A3.4. Management practice at **Estrup** during the 2007 to 2011 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
07/08/2007	Harvest of winterwheat. Stubbleheight 12 cm. Grainyield 81.5 hkg 85% DM
08/08/2007	Straw shredded. Amount 47.4 hkg/ha 100% DM
24/09/2007	Roundup Max (glyphosate) - weeds - 1.5 kg/ha
02/10/2007	Ploughed - depth 20 cm - packed with a ring roller
02/10/2007	Rotarharroved across (seed bed preparation) - depth 4 cm
03/10/2007	Winter wheat sown cv. Frument. depth 4.0 cm rowdistance 12 cm seeding rate 210 kg/ha, final plantnumber 380/m^2.
30/10/2007	Pico 750 WG (picolinafen) - weeds - 0.133 g/ha
22/11/2007	Folicur EC 250 (tebuconazole) - fungi - 1.0 l/ha
13/06/2008	Amistar (azoxystrobin) - fungi - 1.0 l/ha - craks observed
16/08/2008	Harvest of winter wheat. Stubleheight 10 cm, grainyield 83.8 hkg/ha 85% DM, strawyield 40.7 hkg/ha 100% DM
16/08/2008	Straw shredded. Amount 40.7 hkg/ha 100% DM
12/03/2009	Ploughed - depth 18 cm - packed with a ring roller
02/04/2009	Seed bed preparation depth 5 cm
06/04/2009	Tracer (potasium bromide) 30 kg/ha
08/04/2009	Spring barley sown, cv. Keops, seeding rate 182 kg/ha, sowing depth 4.0 cm, row distance 12 cm. Final plantnumber 350/m^2
08/04/2009	Rolled with a cam roller
01/05/2009	Fox 480 SC (bifenox) - weeds - 1.2 l/ha
14/05/2009	Basagran M75 (bentazone+MCPA) - weeds - 1.5 l/ha
04/06/2009	Amistar (azoxystrobin) - fungi - 1.0 l/ha
07/08/2009	Harvest of spring barley. Stuble height 12 cm, grainyield 71.4 hkg/ha 85% DM,
07/08/2009	Straw shredded. Amount 39.9 hkg/ha 100% DM
24/08/2009	Sowing winter rape. Cv. Cabernet, sowing depth 3.0 cm, seeding rate 4 kg/ha , row distance 12.5 cm final plantnumber 86/m^2
24/08/2009	Ploughed - depth 20 cm - packed with a ring roller
24/08/2009	Rotor harrowed - depth 4 cm
25/08/2009	Command CS (Clomazone) - weeds - 0.33 l/ha
30/09/2009	Fox 480 SC (bifenox) - weeds - 0.75 l/ha
09/10/2009	Cyperb (cypermethrin) - pests - 0.15 l/ha
20/04/2010	Due to outwintering field partially sown withspring rape. Cv. Pluto, sowing depth 3.0 cm and 0.5 cm, seeding rate 5,0 kg/ha, row distance 12.0 cm
10/05/2010	Biscaya OD 240 (thiacloprid) - pests- 0.3 l/ha
20/08/2010	Harwest of winter rape. Seed yield 38.3 hkg/ha 91% DM. Straw shredded 41.8 hkg/ha 100% DM. Stubble height 30 cm
23/08/2010	Spring rape shredded 11.64 hkg/ha 100% DM. Stubble height 8 cm
06/09/2010	Rotor harrowed - depth 5 cm
14/09/2010	Winter wheat sown cv. Frument. depth 4.0 cm rowdistance 12 cm seeding rate 210 kg/ha, final plantnumber 370/m^2
14/09/2010	Ploughed - depth 20 cm - packed with a ring roller
14/09/2010	Seedbed preparation - depth 5 cm
30/09/2010	Express ST (tribenuron-methyl) - weeds - 1 tablet/ha
26/04/2011	Fox 480 SC (bifenox) - weeds - 1.2 L/ha
09/05/2011	Flexity (metrafenon) - fungi - 0.5 L/ha
07/06/2011	Flexity (metrafenon) - fungi - 0.5 L/ha

Table A3.5. Management practice at **Faardrup** during the 2007 to 2011 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
10/08/2007	Stuble cultivation - depth 15 cm
22/08/2007	Stuble cultivation - depth 15 cm
18/09/2007	Sowing winter wheat, cv. Ambition - depth 5 cm row distance 13 cm seeding rate 180 kg/ha - final plantnumber 319 m^2
18/09/2007	Ploughed and packed - depth 25 cm
09/10/2007	Stomp SC (pendimethalin) - weeds - 5.0 l/ha
20/11/2007	Folicur 250 (tebuconazole) - fungi - 1.0 l/ha
20/08/2008	Harvest of winter wheat. Grain yield 89.6 hkg 85% DM. Straw yield 65.2 hkg/ha 100% DM stubbleheight 15 cm
26/08/2008	Tracer (potasium bromide), 30 kg/ha
01/12/2008	Ploughing - depth 23 cm
05/04/2009	Sowing sugar beet cv. Palace. depth 3.0 cm row distance 50.0 cm plant distance 20 cm seeding rate 100000 seeds/ha. Final plantnumber 8.5/m^2
05/04/2009	Seed bed preparation - depth 6 cm
24/04/2009	1.5 l/ha Betanal (phenmedipham) + 1.0 l/ha Goliath (metamitron) – weeds
30/04/2009	10 g/ha Safari (triflusulfuron-methyl) + 1.5 l/ha Betanal (phenmedipham) + 1.0 l/ha Goliath (metamitron) + 0.07 l/ha Ethosan (ethofumesate) – weeds
11/05/2009	10 g/ha Safari (triflusulfuron-methyl) + 1.5 l/ha Betanal (phenmedipham) + 1.0 l/ha Goliath (metamitron) + 0.07 l/ha Ethosan (ethofumesate) – weeds
14/05/2009	Focus Ultra (cycloxydim) - weeds -1.0 l/ha
17/06/2009	Focus Ultra (cycloxydim) - weeds -1.0 l/ha
06/10/2009	Harvest of sugar beet. 147.9 hkg/ha 100% root dry matter and 40.1 hkg/ha 100% top dry matter
01/11/2009	Ploughing - depth 20 cm
07/04/2010	Seed bed preparation - depth 6 cm
22/04/2010	Sowing spring barley using a mixture of varieties. Depth 4.5 cm, row distance 12 cm seeding rate 150 kg/ha. Undersown red fescue cv. Maximum, seeding rate 7,0 kg/ha. Depth 2.0 cm row distance 13 cm
01/06/2010	Fighter 480 (bentazone) - weeds - 1.25 l/ha
02/07/2010	Amistar (azoxystrobin) - fungi - 1.0 l/ha (not analyzed)
21/08/2010	Harvest of spring barley. Grain yield 58.5 hkg 85% DM.
21/08/2010	Straw removed. Straw yield 27.5 hkg/ha 100% DM. Stubbleheight 10 cm
25/10/2010	Fox 480 SC (bifenox) - weeds - 1.5 l/ha
21/05/2011	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 l/ha

Appendix 4

Precipitation data for the PLAP sites
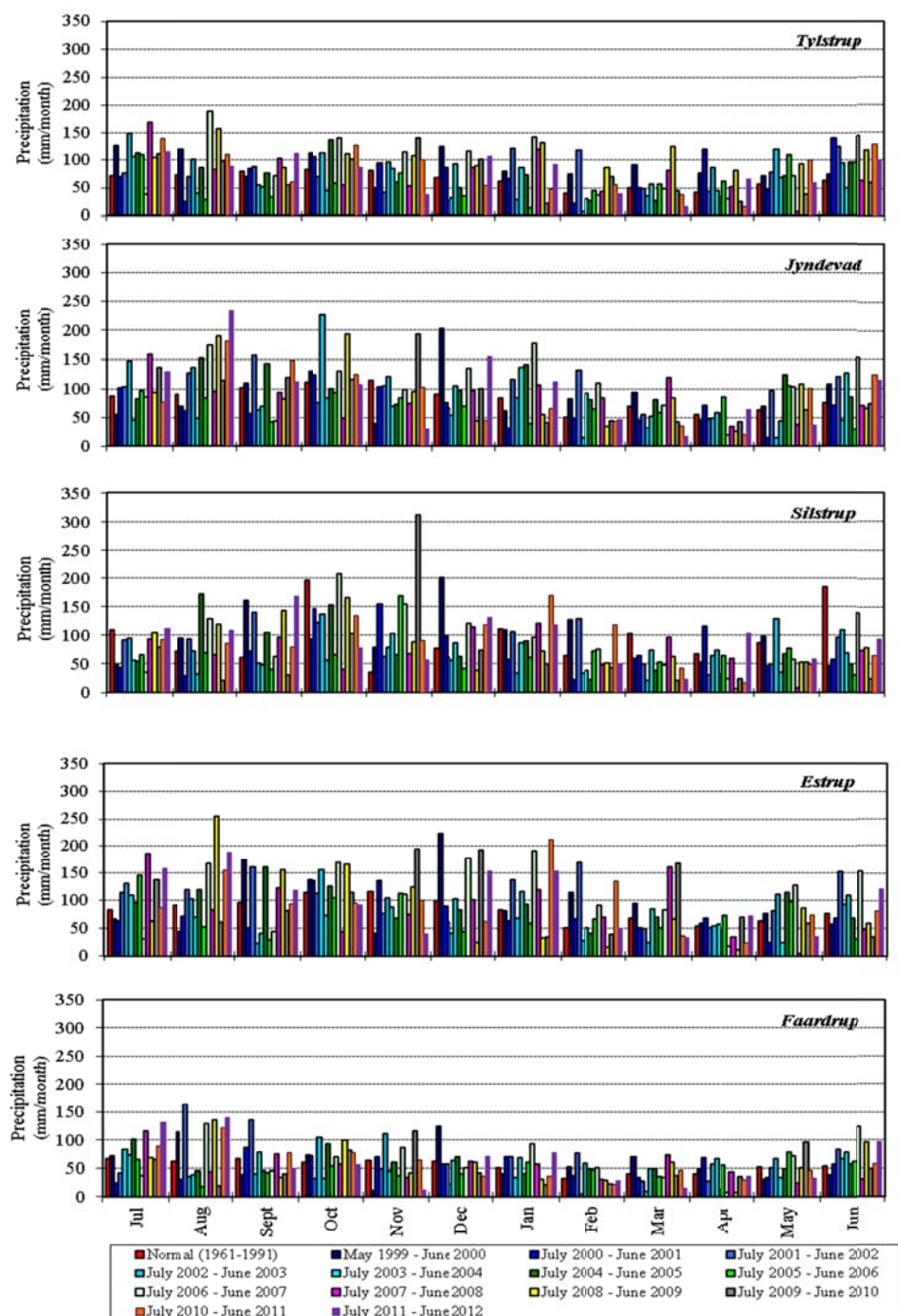
Figure A4.1. Monthly precipitation at all localities for the monitoring period July 2000–June 2012. Normal values (1961–1990) are included for comparison.

Appendix 5

Pesticide detections in samples for drains, suction cups and groundwater monitoring wells

Table A5.1. Number of samples where pesticides were either not detected (nd), detected in concentrations below 0.1 µg/L (<0.1 µg/L) or detected in concentrations above 0.1 µg/L (≥ 0.1 µg/L) at **Tylstrup**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included.

			Vertical			Suction cups	
Parent	Compound	nd	< 0.1µg/L	≥ 0.1µg/L	nd	< 0.1µg/L	≥ 0.1µg/L
Aclonifen	Aclonifen	123			68		
Azoxystrobin	Azoxystrobin	216	-	-	95	-	-
	CyPM	216	-	-	95	-	-
Bentazone	2-amino-N-isopropyl-benzamide	191	-	-	72	-	-
	Bentazone	330	-	-	136	1	-
Boscalid	Boscalid	74	-	-	40	-	-
Bromoxynil	Bromoxynil	192	-	-	72	-	-
Clomazone	Clomazone	230	-	-	82	-	-
	FMC 65317	208	-	-	74	-	-
Clopyralid	Clopyralid	83	-	-	81	-	-
Cyazofamid	Cyazofamid	123	-	-	68	-	-
Dimethoate	Dimethoate	176	-	-	65	-	-
Epoxiconazole	Epoxiconazole	199	-	-	74	-	-
Fenpropimorph	Fenpropimorph	313	-	-	89	-	-
	Fenpropimorph acid	276	-	-	75	-	-
Flamprop-M-isopropyl	Flamprop	176	-	-	65	-	-
	Flamprop-M-isopropyl	176	-	-	65	-	-
Fluazifop-P-butyl	Fluazifop-P	178	-	-	65	-	-
	TFMP	3	-	-			
Fluroxypyr	Fluroxypyr	194	-	-	70	-	-
Ioxynil	Ioxynil	198	-	-	72	-	-
Linuron	Linuron	271	-	-	67	-	-
Mancozeb	ETU	198	2	-	37	7	-
Metalaxyl-M	CGA 108906	7	84	40	16	25	25
	CGA 62826	124	7	-	51	14	1
	Metalaxyl-M	122	9	-	64	4	-
Metribuzin	Desamino-diketo-metribuzin	289	231	5	168	30	51
	Desamino-metribuzin	366	-	-	87	-	-
	Diketo-metribuzin	73	138	315	81	192	61
	Metribuzin	387	1	-	89	2	-
Pendimethalin	Pendimethalin	436	-	-	144	-	-
Pirimicarb	Pirimicarb	301	-	-	82	-	-
	Pirimicarb-desmethyl	301	-	-	81	-	-
	Pirimicarb-desmethyl-formamido	173	-	-	52	-	-
Propiconazole	Propiconazole	313	-	-	89	-	-
Propyzamide	Propyzamide	221	-	-	82	-	-
	RH-24580	221	-	-	82	-	-
	RH-24644	221	-	-	82	-	-
	RH-24655	157	-	-	58	-	-

Parent	Compound	Vertical			Suction cups		
		nd	< 0.1µg/L	≥ 0.1µg/L	nd	< 0.1µg/L	≥ 0.1µg/L
Rimsulfuron	PPU	578	41	-	74	175	3
	PPU-desamino	614	5	-	199	53	-
	Rimsulfuron	178	-	-	65	-	-
Tebuconazole	Tebuconazole	195	1	-	77	-	-
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	190	1	-	67	5	-
	Desethyl-terbuthylazine	191	-	-	70	2	-
	Desisopropylatrazine	190	1	-	55	17	-
	Hydroxy-terbuthylazine	191	-	-	71	1	-
	Terbuthylazine	179	-	-	72	-	-
Thiamethoxam	CGA 322704	175	-	-	64	-	-
	Thiamethoxam	175	-	-	64	-	-
Triasulfuron	Triasulfuron	301	-	-	82	-	-
	Triazinamin	291	-	-	76	-	-
Tribenuron-methyl	Triazinamin-methyl	446	-	-	138	-	-

Table A5.2. Number of samples where pesticides were either not detected (nd), detected in concentrations below 0.1 µg/L (<0.1 µg/L) or detected in concentrations above 0.1 µg/L (>=0.1 µg/L) at **Jyndevad**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included.

		Vertical			Suction cups		
Parent	Compound	nd	< 0.1µg/L	≥ 0.1µg/L	nd	< 0.1µg/L	≥ 0.1µg/L
Aclonifen	Aclonifen	131			32		
Amidosulfuron	Amidosulfuron	88	-	-	20	2	1
	Desmethyl-amidosulfuron	88	-	-	23	-	-
Azoxystrobin	Azoxystrobin	233	-	-	65	-	-
	CyPM	233	-	-	65	-	-
Bentazone	2-amino-N-isopropyl-benzamide	178	-	-	45	2	-
	Bentazone	449	-	-	85	34	5
Bifenox	Bifenox	216	2	-	54	2	-
	Bifenox acid	166	-	-	52	1	-
	Nitrofen	218	-	-	56	-	-
Bromoxynil	Bromoxynil	218	-	-	61	-	-
Chlormequat	Chlormequat	14	-	-	28	-	-
Cyazofamid	Cyazofamid	131	-	-	32	-	-
Diflufenican	AE-05422291	79	-	-	15	-	-
	AE-B107137	79	-	-	30	-	-
	Diflufenican	79	-	-	15	-	-
Dimethoate	Dimethoate	190	-	-	52	-	-
Epoxiconazole	Epoxiconazole	323	1	-	90	-	-
Fenpropimorph	Fenpropimorph	257	1	-	78	1	-
	Fenpropimorph acid	264	-	-	79	-	-
Florasulam	Florasulam	191	-	-	54	-	-
	Florasulam-desmethyl		-	-	28	-	-
Fluazifop-P-butyl	Fluazifop-P	190	-	-	51	-	-
	TFMP	3	-	-			
Fluroxypyr	Fluroxypyr	193	-	-	55	-	-
Glyphosate	AMPA	221	2	-	71	1	-
	Glyphosate	223	-	-	72	-	-
Ioxynil	Ioxynil	218	-	-	61	-	-
MCPA	2-methyl-4-chlorophenol	210	-	-	56	-	-
	MCPA	210	-	-	56	-	-
Mesosulfuron-methyl	Mesosulfuron	12	-	-	45	-	-
	Mesosulfuron-methyl	285	-	-	78	-	-
Metalaxyl-M	CGA 108906	14	65	54	2	9	33
	CGA 62826	100	33	-	4	20	20
	Metalaxyl-M	120	3	10	22	10	-
Metribuzin	Desamino-diketo-metribuzin	6	7	13	6	-	-
	Desamino-metribuzin	26	-	-	4	-	-
	Diketo-metribuzin	-	7	19	3	3	-
	Metribuzin	26	-	-	6	-	-
Pendimethalin	Pendimethalin	257	-	-	71	-	-
Picolinafen	CL153815	35	-	-	36	-	-
	Picolinafen	35	-	-	35	1	-
Pirimicarb	Pirimicarb	251	-	-	69	-	-
	Pirimicarb-desmethyl	251	-	-	68	1	-
	Pirimicarb-desmethyl-formamido	251	-	-	69	-	-
Propiconazole	Propiconazole	291	-	-	87	-	-
Pyridate	PHCP	184	-	-	59	-	-
	Pyridate	116	-	-	39	-	-
Rimsulfuron	PPU	486	336	4	39	122	60

Parent	Compound	Vertical			Suction cups		
		nd	< 0.1μg/L	≥ 0.1μg/L	nd	< 0.1μg/L	≥ 0.1μg/L
	PPU-desamino	742	84	-	110	105	6
	Rimsulfuron	189	-	-	52	-	-
Tebuconazole	Tebuconazole	213	1	-	58	-	-
Terbuthylazine	Desethyl-terbuthylazine	490	27	-	130	20	-
	Terbuthylazine	260	-	-	79	-	-
Tribenuron-methyl	Triazinamin-methyl	252	-	-	77	-	-

Table A5.3. Number of samples where pesticides were either not detected (nd), detected in concentrations below 0.1 µg/L (<0.1) or detected in concentrations above 0.1 µg/L (>=0.1) at **Silstrup**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included.

Parent	Compound	Drainage			Horizontal			Vertical			Suction cups		
		nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1
Amidosulfuron	Amidosulfuron	1											
	Desmethyl-amidosulfuron	1	-	-									
Azoxystrobin	Azoxystrobin	89	10	-	122	-	-	234	-	-			
	CyPM	44	74	4	151	8	-	289	20	-			
Bentazone	2-amino-N-isopropyl-benzamide	65	-	-	74	-	-	131	-	-			
	Bentazone	75	40	5	133	8	1	244	18	2			
Bifenox	Bifenox	47	3	2	51	-	-	98	5	-			
	Bifenox acid	22	2	18	42	3	6	85	3	14			
	Nitrofen	47	2	3	51	-	-	103	-	-			
Bromoxynil	Bromoxynil	1	-	-									
Chlormequat	Chlormequat	20	1	-	36	-	-	66	-	-			
Clopyralid	Clopyralid	44	-	-	67	-	-	124	-	-			
Desmedipham	Desmedipham	101	-	-	107	1	-	240	-	-	58	-	-
	EHPC	74	-	-	68	-	-	139	-	-	26	-	-
Dimethoate	Dimethoate	81	-	1	73	1	-	148	-	-	27	-	-
Epoxiconazole	Epoxiconazole	36	-	-	62	-	-	117	-	-			
Ethofumesate	Ethofumesate	127	14	1	169	2	-	355	3	-	54	3	2
Fenpropimorph	Fenpropimorph	82	-	-	74	-	-	148	-	-	27	-	-
	Fenpropimorph acid	81	1	-	74	-	-	148	-	-	27	-	-
Flamprop-M-isopropyl	Flamprop	74	7	-	74	-	-	148	-	-	27	-	-
	Flamprop-M-isopropyl	70	11	1	73	1	-	148	-	-	27	-	-
Fluazifop-P-butyl	Fluazifop-P	116	-	-	140	1	-	301	-	-	59	-	-
	TFMP	40	9	20	74	11	2	124	31	11			
Fluroxypyr	Fluroxypyr	50	-	-	74	-	-	142	-	-			
Glyphosate	AMPA	25	108	14	123	5	-	226	10	-	8	-	-
	Glyphosate	79	52	15	128	-	-	232	4	-	8	-	-
Iodosulfuron-methyl	Iodosulfuron-methyl	60	-	-	85	-	-	165	-	-			
	Metsulfuron-methyl	60	-	-	85	-	-	165	-	-			
Ioxynil	Ioxynil	1	-	-									
MCPA	2-methyl-4-chlorophenol	51	-	-	67	-	-	124	-	-			
	MCPA	51	-	-	67	-	-	123	-	-			
Metamitron	Desamino-metamitron	97	42	3	165	3	3	334	23	1	40	15	4
	Metamitron	111	28	3	161	10	-	339	17	2	40	10	8
Pendimethalin	Pendimethalin	91	14	-	122	-	-	222	-	-			
Phenmedipham	3-aminophenol	56	-	-	72	-	-	173	-	-	53	-	-
	MHPC	101	-	-	108	-	-	240	-	-	59	-	-
	Phenmedipham	101	-	-	108	-	-	240	-	-	59	-	-
Pirimicarb	Pirimicarb	160	14	-	210	-	-	433	3	-	59	-	-
	Pirimicarb-desmethyl	173	1	-	210	-	-	436	-	-	59	-	-
	Pirimicarb-desmethyl-formamido	141	-	-	160	-	-	308	-	-	20	-	-
Propiconazole	Propiconazole	76	6	-	74	-	-	148	-	-	27	-	-
Propyzamide	Propyzamide	43	17	6	75	2	1	143	5	1			
	RH-24580	64	2	-	78	-	-	149	-	-			
	RH-24644	51	15	-	77	1	-	148	1	-			
	RH-24655	66	-	-	78	-	-	149	-	-			

Parent	Compound	Drainage			Horizontal			Vertical			Suction cups		
		nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1
Prosulfocarb	Prosulfocarb	69	4	1	78	1	-	147	-	-			
Pyridate	PHCP	62	-	4	66	2	-	109	8	4			
Rimsulfuron	PPU	1	-	-									
	PPU-desamino	1	-	-									
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	43	27	1	84	-	-	151	1	-			
	Desethyl-terbuthylazine	8	64	44	101	32	-	113	127	2			
	Desisopropylatrazine	28	43	-	84	-	-	148	4	-			
	Hydroxy-terbuthylazine	45	26	-	84	-	-	152	-	-			
	Terbuthylazine	31	51	9	107	5	-	173	30	1			
Triasulfuron	Triazinamin	46	-	-	77	-	-	146	-	-			
Tribenuron-methyl	Triazinamin-methyl	82	-	-	74	-	-	148	-	-	27	-	-
Triflusulfuron-methyl	IN-D8526	32	-	-	56	-	-	102	-	-			
	IN-E7710	27	5	-	56	-	-	102	-	-			
	IN-M7222	32	-	-	55	1	-	102	-	-			
	Triflusulfuron-methyl	32	-	-	56	-	-	102	-	-			

Table A5.4. Number of samples where pesticides were either not detected (nd), detected in concentrations below 0.1 µg/L (<0.1 µg/L) or detected in concentrations above 0.1 µg/L (>=0.1 µg/L) at **Estrup**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included.

Parent	Compound	Drainage			Horizontal			Vertical			Suction cups		
		nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥ 0.1	nd	<0.1	≥0.1
Amidosulfuron	Amidosulfuron	100			34			109					
Azoxystrobin	Azoxystrobin	160	93	14	128	1	-	388	1	-			
	CyPM	35	126	106	119	10	-	384	5	-			
Bentazone	2-amino-N-isopropyl-benzamide	237		-	79	1	-	271	-	-	5	-	-
	Bentazone	177	145	12	122	15	-	439	1	-	3	2	2
Bifenox	Bifenox	71	2	1	52	-	-	115	-	-			
	Bifenox acid	69	5	9	52	-	-	115	-	1			
	Nitrofen	74	-	-	52	-	-	115	-	-			
Bromoxynil	Bromoxynil	136	1	2	41	-	-	125	-	-	3	-	-
Chlormequat	Chlormequat	45	1	-	18	-	-	56	-	-			
Clopyralid	Clopyralid	1	-	-									
Dimethoate	Dimethoate	88	-	-	42	-	-	158	-	-	23	-	-
Epoxiconazole	Epoxiconazole	35	12	2	19	-	-	69	-	-			
Ethofumesate	Ethofumesate	91	27	8	46	-	-	158	-	-			
Fenpropimorph	Fenpropimorph	82	1	-	39	-	-	150	-	-	23	-	-
	Fenpropimorph acid	83	-	-	34	-	-	124	-	-	20	-	-
Flamprop-M-isopropyl	Flamprop	119	13	-	55	-	-	208	-	-	23	-	-
	Flamprop-M-isopropyl	112	20	-	55	-	-	208	-	-	23	-	-
Florasulam	Florasulam	92	-	-	35	-	-	125	-	-			
	Florasulam-desmethyl	81	-	-	30	-	-	100	-	-			
Fluroxypyr	Fluroxypyr	87	1	2	34	-	-	120	1	-			
Glyphosate	AMPA	57	286	107	192	1	-	610	7	-	23	-	-
	Glyphosate	177	173	100	187	4	1	576	37	3	23	-	-
Iodosulfuron-methyl	Metsulfuron-methyl	131	-	-	55	-	-	208	-	-	22	1	-
Ioxynil	Ioxynil	119	15	5	41	-	-	125	-	-	3	-	-
MCPA	2-methyl-4-chlorophenol	102	1	-	34	-	-	112	-	-			
	MCPA	91	10	2	34	-	-	111	1	-			
Mesosulfuron-methyl	Mesosulfuron	74	-	-	24	-	-	83	-	-			
	Mesosulfuron-methyl	62	13	-	27	-	-	99	-	-			
Metamitron	Desamino-metamitron	76	38	11	46	-	-	157	-	-			
	Metamitron	81	27	15	46	-	-	158	-	-			
Metrafenone	Metrafenone	12	18	-	23	-	-	45	-	-			
Pendimethalin	Pendimethalin	119	4	-	41	-	-	147	-	-	7	-	-
Picolinafen	CL153815	50	20	11	40	-	-	118	-	-			
	Picolinafen	64	17	-	40	-	-	118	-	-			
Pirimicarb	Pirimicarb	159	40	-	67	-	-	225	1	-	6	-	-
	Pirimicarb-desmethyl	192	-	-	66	-	-	223	-	-	6	-	-
	Pirimicarb-desmethyl-formamido	199	13	13	76	-	-	261	-	-	5	-	-
Propiconazole	Propiconazole	192	23	3	86	-	-	309	2	-	23	-	-
Tebuconazole	Tebuconazole	40	24	17	39	-	-	118	3	2			
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	44	63	24	50	-	-	180	-	-			
	Desethyl-terbuthylazine	18	111	35	59	7	-	232	-	-			
	Desisopropylatrazine	90	70	1	62	1	-	197	26	-			
	Hydroxy-terbuthylazine	43	72	16	50	-	-	180	-	-			
	Terbuthylazine	49	78	34	63	-	-	222	1	-			

| Parent	Compound	Drainage			Horizontal			Vertical			Suction cups		
		nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1
Thiacloprid	M34	55	-	-	34	-	-	66	-	-			
	Thiacloprid	47	-	-	34	-	-	66	-	-			
	Thiacloprid sulfonic acid	56	-	-	34	-	-	66	-	-			
	Thiacloprid-amide	46	1	-	34	-	-	66	-	-			
Triasulfuron	Triazinamin	131	-	-	56	-	-	203	1	-	22	-	-
Tribenuron-methyl	Triazinamin-methyl	46	2	-	34	-	-	67	-	-	1	-	-

Table A5.5. Number of samples where pesticides were either not detected (nd), detected in concentrations below 0.1 µg/L (<0.1 µg/L) or detected in concentrations above 0.1 µg/L (>=0.1µg/L) at **Faardrup**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included.

Parent	Compound	Drainage			Horizontal			Vertical			Suction cups		
		nd	<0.1	≥ 0.1	nd	<0.1	≥ 0.1	nd	<0.1	≥ 0.1	nd	<0.1	≥ 0.1
Azoxystrobin	Azoxystrobin	106	-	-	92	-	-	194	-	-			
	CyPM	102	4	-	92	-	-	194	-	-			
Bentazone	2-amino-N-isopropyl-benzamide	67	1	-	61	-	-	132	-	-			
	Bentazone	122	14	6	92	5	1	213	4	3			
Bifenox	Bifenox	56	6	-	30	-	-	74	-	-			
	Bifenox acid	24	1	17	30	-	1	73	-	-			
	Nitrofen	56	5	1	30	-	-	74	-	-			
Bromoxynil	Bromoxynil	101	-	-	81	-	-	225	-	-	73	-	-
Clomazone	Clomazone	84	-	1	69	-	-	166	-	-			
	FMC 65317	84	-	1	69	-	-	166	-	-			
Desmedipham	Desmedipham	99	-	-	66	-	-	166	-	-	29	-	-
	EHPC	83	-	-	52	-	-	124	-	-	16	-	-
Dimethoate	Dimethoate	77	-	-	58	-	-	149	-	-			
Epoxiconazole	Epoxiconazole	81	-	-	66	-	-	143	-	-			
Ethofumesate	Ethofumesate	150	7	6	104	-	-	227	25	6	27	2	-
Fenpropimorph	Fenpropimorph	101	-	-	80	1	-	225	-	-	73	-	-
	Fenpropimorph acid	101	-	-	81	-	-	225	-	-	73	-	-
Flamprop-M-isopropyl	Flamprop	76	1	-	58	-	-	149	-	-			
	Flamprop-M-isopropyl	70	1	-	56	-	-	143	-	-			
Fluazifop-P-butyl	Fluazifop-P	123	5	3	87	-	-	206	5	1	26	3	-
	Fluazifop-P-butyl	99	-	-	66	-	-	166	-	-	29	-	-
	TFMP	40	-	-	25	-	-	55	-	-			
Fluroxypyr	Fluroxypyr	182	-	1	146	1	-	368	-	-	73	-	-
Glyphosate	AMPA	160	9	1	126	-	-	315	2	-	58	5	-
	Glyphosate	166	4	-	125	1	-	313	4	-	62	1	-
Ioxynil	Ioxynil	99	1	-	81	-	-	224	1	-	73	-	-
MCPA	2-methyl-4-chlorophenol	142	-	1	109	-	-	256	-	-			
	MCPA	141	1	1	109	-	-	256	-	-			
Metamitron	Desamino-metamitron	147	12	4	104	-	-	210	36	12	29	-	-
	Metamitron	151	10	2	104	-	-	234	20	4	29	-	-
Pendimethalin	Pendimethalin	55	2	-	55	-	-	125	-	-			
Phenmedipham	MHPC	97	1	1	66	-	-	165	1	-	29	-	-
	Phenmedipham	99	-	-	66	-	-	164	2	-	29	-	-
Pirimicarb	Pirimicarb	148	7	-	116	-	-	319	2	-	73	-	-
	Pirimicarb-desmethyl	94	6	-	66	-	-	163	3	-	29	-	-
	Pirimicarb-desmethyl-formamido	97	3	-	66	-	-	164	2	-	29	-	-
Propiconazole	Propiconazole	178	-	-	138	-	-	372	1	-	73	-	-
Propyzamide	Propyzamide	70	2	2	68	1	-	155	-	-			
	RH-24580	74	-	-	69	-	-	155	-	-			
	RH-24644	70	4	-	69	-	-	155	-	-			
	RH-24655	73	1	-	69	-	-	155	-	-			
Prosulfocarb	Prosulfocarb	78	-	-	61	-	-	126	-	-			
Tebuconazole	Tebuconazole	50	4	-	53	-	-	120	1	-			

Parent	Compound	Drainage			Horizontal			Vertical			Suction cups		
		nd	<0.1	≥ 0.1	nd	<0.1	≥ 0.1	nd	<0.1	≥ 0.1	nd	<0.1	≥ 0.1
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	60	7	1	60	1	-	126	6	-			
	Deset8hyl-terbuthylazine	21	82	7	68	21	-	149	15	30			
	Desisopropylatrazine	85	24	1	57	32	-	166	28	-			
	Hydroxy-terbuthylazine	89	20	1	85	4	-	164	30	-			
	Terbuthylazine	69	30	11	83	5	1	149	25	20			
Thiamethoxam	CGA 322704	68	-	-	58	-	-	126	-	-			
	Thiamethoxam	68	-	-	58	-	-	126	-	-			
Tribenuron-methyl	Triazinamin-methyl	77	-	-	57	-	-	148	-	-			
Triflusulfuron-methyl	IN-D8526	63	-	-	38	-	-	92	-	-			
	IN-E7710	63	-	-	38	-	-	92	-	-			
	IN-M7222	63	-	-	38	-	-	92	-	-			
	Triflusulfuron-methyl	63	-	-	38	-	-	92	-	-			

Appendix 6

Laboratory internal control cards
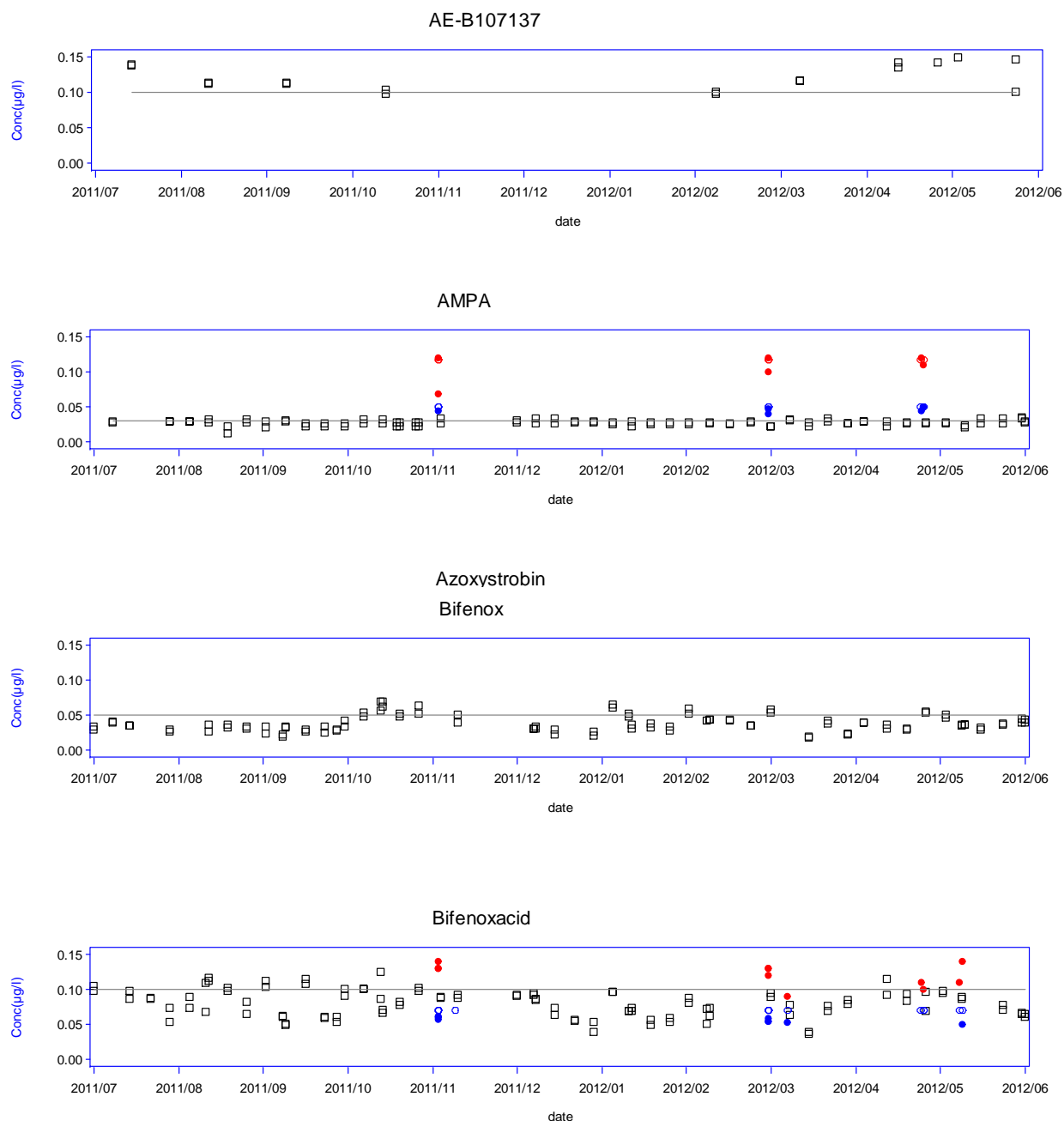
Figure A6.1. Quality control data for pesticide analysis by laboratory 1. <u>Internal laboratory control</u> samples are indicated by square symbols and the nominal level is indicated by the solid grey line (■ IQ measured, — IQ nominal concentration). <u>External control</u> samples are indicated by circles. Open circles indicate the nominal level (○ EQ nominal low, ○EQ nominal high), and closed circles the observed concentration (● EQ measured low, ● EQ measured high).

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. <u>Internal laboratory control</u> samples are indicated by square symbols and the nominal level is indicated by the solid grey line (■IQ measured, — IQ nominal concentration). <u>External control</u> samples are indicated by circles. Open circles indicate the nominal level (○ EQ nominal low, ○ EQ nominal high), and closed circles the observed concentration (● EQ measured low, ● EQ measured high).

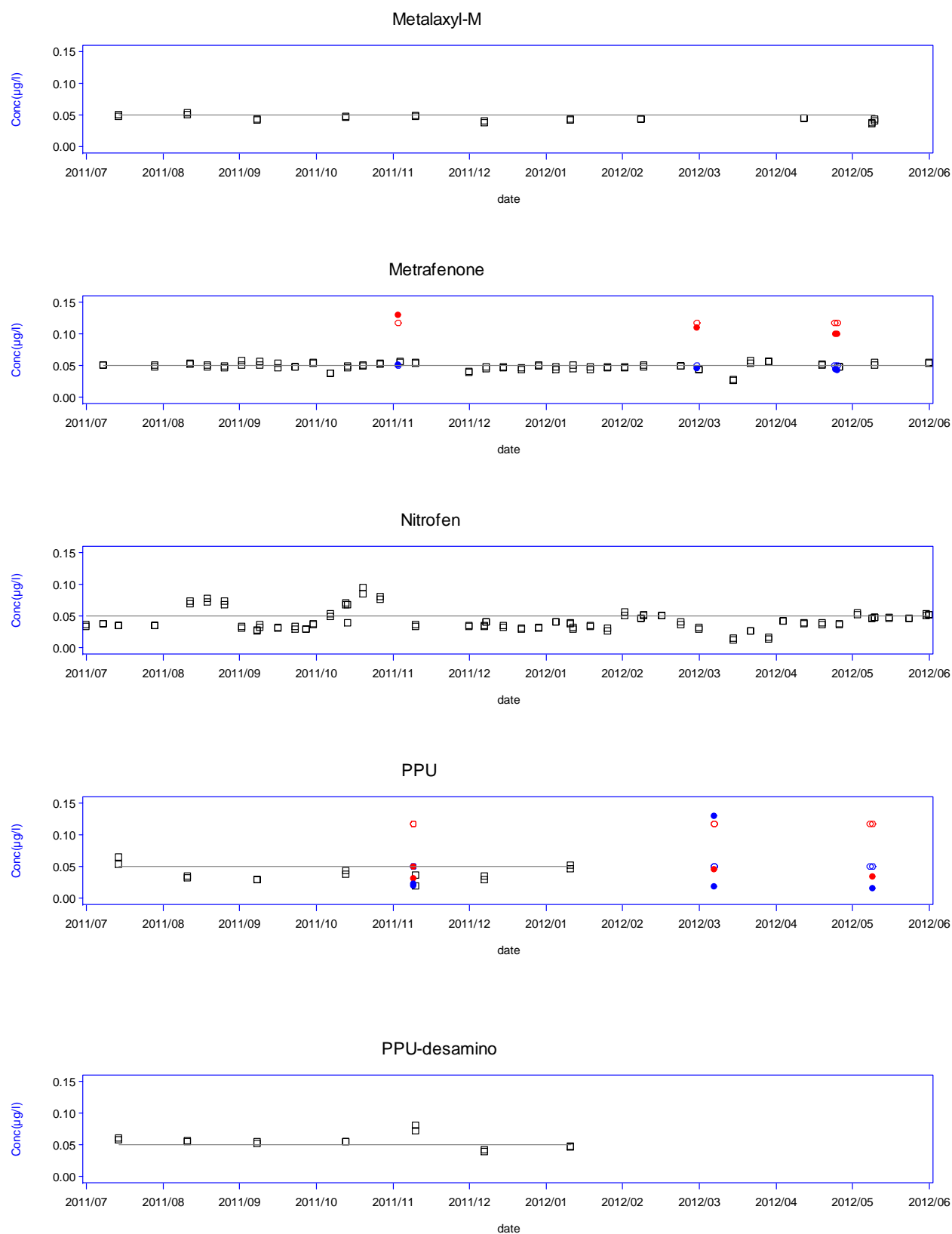**Figure A6.1 continued.** Quality control data for pesticide analysis by laboratory 1. <u>Internal laboratory control</u> samples are indicated by square symbols and the nominal level is indicated by the solid grey line (■IQ measured, — IQ nominal concentration). <u>External control</u> samples are indicated by circles. Open circles indicate the nominal level (O EQ nominal low, O EQ nominal high), and closed circles the observed concentration (● EQ measured low, ● EQ measured high).
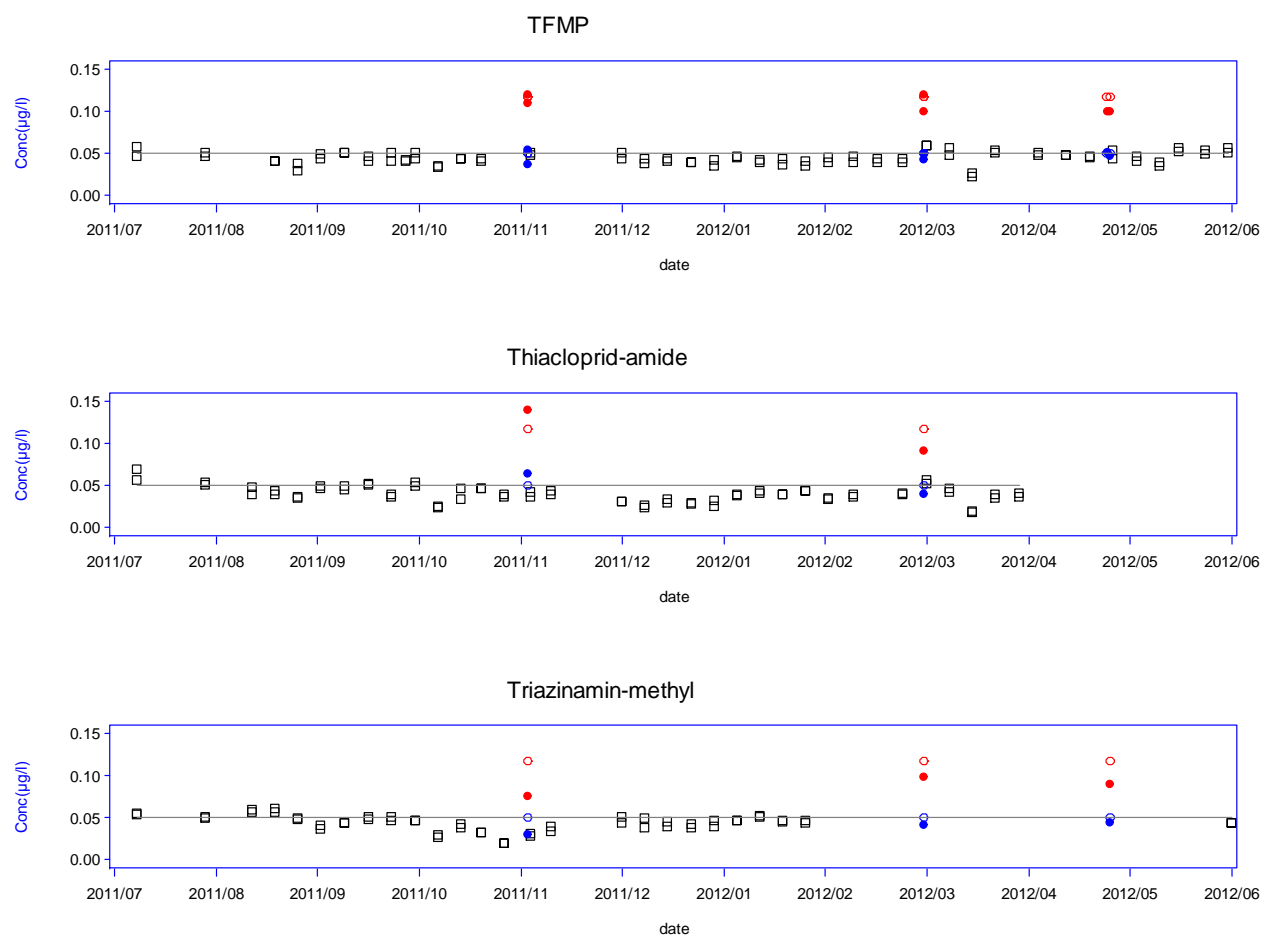
Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. <u>Internal laboratory control</u> samples are indicated by square symbols and the nominal level is indicated by the solid grey line (■ IQ measured, — IQ nominal concentration). <u>External control</u> samples are indicated by circles. Open circles indicate the nominal level (O EQ nominal low, O EQ nominal high), and closed circles the observed concentration (● EQ measured low, ● EQ measured high).

Appendix 7

Pesticides analysed at 5 PLAP sites in the period up to 2007

Table A7.1. Pesticides analysed at **Tylstrup** with the products used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after the application. C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. (See Appendix 2 for calculation method).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Potatoes 1999						
Linuron (Afalon)	May 99	Jul 01	2550	1253	87	<0.01
- *ETU*[1] (Dithane DG)	Jun 99	Oct 01	2381	1169	73	<0.01
Metribuzine (Sencor WG)	Jun 99	Jul 03	4223	2097	85	<0.01
- *metribuzine-diketo*		Jul 10†	11142	5387	85	0.05–0.36
- *metribuzine-desamino*		Jul 03	4223	2097	85	<0.02
- *metribuzine-desamino-diketo*		Apr 08	8689	4192	85	0.14–0.97
Spring barley 2000						
Triasulfuron (Logran 20 WG)	May 00	Apr 03	2740	1283	13	<0.02
- *triazinamin*						<0.02
Propiconazole (Tilt Top)	Jun 00	Jul 03	2948	1341	11	<0.01
Fenpropimorph (Tilt Top)	Jun 00	Jul 03	2948	1341	11	<0.01
- *fenpropimorphic acid*						<0.02
Pirimicarb (Pirimor G)	Jun 00	Apr 03	2622	1263	17	<0.01
- *pirimicarb-desmethyl*						<0.02
- *pirimicarb-desmethyl-formamido*						<0.02
Winter rye 2001						
Pendimethalin (Stomp SC)	Nov 00	Apr 03	2271	1219	109	<0.01
Triazinamin-methyl [2] (Express)	Nov 00	Apr 03	2271	1219	109	<0.02
Propiconazole (Tilt Top)	May 01	Jul 03	2948	1341	11	<0.01
Fenpropimorph (Tilt Top)	May 01	Jul 03	2948	1341	11	<0.01
- *fenpropimorphic acid*						<0.01
Winter rape 2002						
Clomazone (Command CS)	Sep 01	Jul 04	2534	1194	9	<0.01
- *FMC65317 (propanamide-clomazone)*						<0.02
Winter wheat 2003						
Bromoxynil (Oxitril CM)	Oct 02	Apr 05	2082	995	53	<0.01
Ioxynil (Oxitril CM)	Oct 02	Apr 05	2082	995	53	<0.01
Fluroxypyr (Starane 180)	May 03	Jul 05	1867	787	50	<0.02
Flamprop-M-isopropyl (Barnon Plus 3)	May 03	Jul 05	2635	1031	42	<0.01
- *Flamprop-M (free acid)*						
Dimethoate (Perfekthion 500 S)	Jul 03	Jul 05	1629	722	14	<0.01
Potatoes 2004						
-*Fluazifop-P (free acid)*[3] (Fusilade X-tra)	May 04	Jul 06	1754	704	16	<0.01
- *PPU*[4] (Titus)	Jun 04	Jul 10†	6211	3008	13	<0.01[5]
- *PPU-desamino*[4] (Titus)	Jun 04	Jul 10†	6211	3008	13	<0.01[5]
Maize 2005						
Terbuthylazine (Inter-Terbutylazine)	May 05	Jul 07	2145	933	16	<0.01
-*desethyl-terbuthylazine*						<0.01
-*2-hydroxy-terbuthylazine*						<0.01
-*desisopropyl-atrazine*						<0.01[6]
-*2-hydroxy-desethyl-terbuthylazine*						<0.01
Bentazone (Laddok TE)	Jun 05	Jul 07	2061	927	33	<0.01
-*AIBA*						<0.01
Spring barley 2006						
-*triazinamin-methyl*[7] (Express ST)	Jun 06	Jul 08	2349	1184	43	<0.02
Epoxiconazole (Opus)	Jul 06	Jul 08	2233	1148	24	<0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.

[1] *Degradation product of mancozeb. The parent compound degrades too rapidly to be detected by monitoring.*

[2] *Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.*

[3] *Degradation product of fluazifop-P-butyl. The parent compound degrades too rapidly to be detected by monitoring.*

[4] *Degradation product of rimsulfuron. The parent compound degrades too rapidly to be detected by monitoring.*

[5] *Leaching increased the second and third year after application.*

[6] *Leaching increased during the second year after application but measured concentrations did not exceed 0.042 µg/L (see Kjær et al., 2008).*

[7] *Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.*

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2009.

Table A7.2. Pesticides analysed at **Jyndevad** with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration 1 m b.g.s.the first year after application. (See Appendix 2 for calculation method).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (μg/L)
Winter rye 2000						
Glyphosate (Roundup 2000)	Sep 99	Apr 02	2759	1607	139	<0.01
- AMPA						<0.01
Triazinamin-methyl[1] (Express)	Nov 99	Apr 02	2534	1451	86	<0.02
Propiconazole (Tilt Top)	Apr 00	Jul 02	2301	1061	3	<0.01
Fenpropimorph (Tilt Top)	Apr 00	Apr 02	2015	1029	3	<0.01
- fenpropimorphic acid						<0.01
Maize 2001						
Terbuthylazine (Lido 410 SC)	May 01	Apr 04	3118	1809	4	<0.01
- desethyl-terbuthylazine	May 01	Apr 07	6742	3826	4	<0.01-0.02
PHCP[2] (Lido 410 SC)	May 01	Jul 03	2413	1366	4	<0.02
Potatoes 2002						
- PPU (Titus)[3]	May 02	Jul 10†	9389	5126	11	0.06[4]-0.13
- PPU-desamino (Titus)[3]		Jul 10†	9389	5126	11	0.01-0.03
Spring barley 2003						
MCPA (Metaxon)	Jun 03	Jul 05	2340	1233	0	<0.01
- 4-chlor,2-methylphenol						<0.01
Dimethoate (Perfekthion 500 S)	Jun 03	Jul 05	2278	1232	1	<0.01
Pea 2004						
Bentazone (Basagran 480)	May 04	Jul 07	3888	2044	4	0.02-0.13
- AIBA						<0.01
Pendimethalin (Stomp SC)	May 04	Apr 07	3557	1996	4	<0.01
Pirimicarb (Pirimor G)	Jun 04	Apr 07	3493	1993	27	<0.01
- Pirimicarb-desmethyl						<0.01
-Pirimicarb-desmethyl-						<0.02
- fluazifop-P(free acid)[5] (Fusilade X-tra)	Jun 04	Jul 06	2395	1233	27	<0.01
Winter wheat 2005						
Ioxynil (Oxitril CM)	Oct 04	Apr 07	2955	1791	81	<0.01
Bromoxynil (Oxitril CM)	Oct 04	Apr 07	2955	1791	81	<0.01
Amidosulfuron (Gratil 75 WG)	Apr 05	Jul 07	1070	515	33	<0.01
Fluroxypyr (Starane 180 S)	May 05	Jul 07	2683	1360	37	<0.02
Azoxystrobin (Amistar)	May 05	Apr 07	2274	1283	49	<0.01
- CyPM						<0.02
Spring barley 2006						
Florasulam (Primus)	May 06	Jul 08	2779	1487	34	<0.01
- florasulam-desmethyl						<0.03
Epoxiconazole (Opus)	Jun 06	Dec 09	4698	2592	31	<0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.

[1] *Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.*

[2] *Degradation product of pyridate. The parent compound degrades too rapidly to be detected by monitoring.*

[3] *Degradation product of rimsulfuron. The parent compound degrades too rapidly to be detected by monitoring.*

[4] *Leaching increased the second year after application.*

[5] *Degradation product of fluazifop-P-butyl. The parent compound degrades too rapidly to be detected by monitoring.*

† *Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2009.*

Table A7.3. Pesticides analysed at **Silstrup** with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application. (See Appendix 2 for calculation methods).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Fodder beet 2000						
Metamitron (Goltix WG)	May 00	Apr 03	2634	1328	53	0.05
- *metamitron-desamino*						0.06
Ethofumesate (Betanal Optima)	May 00	Apr 03	2634	1328	53	0.03
Desmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	53	<0.01
- *EHPC*						<0.02
Phenmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	53	<0.01
- *MHPC*						<0.02
- *3-aminophenol*						<0.02
Fluazifop-P-butyl (Fusilade X-tra)	Jun 00	Jul 02	1953	1019	5	<0.01
- *fluazifop (free acid)*						<0.02
Pirimicarb (Pirimor G)	Jul 00	Jul 07	6452	2825	1	<0.01
- *pirimicarb-desmethyl*						<0.01
- *pirimicarb-desmethyl-formamido*						<0.02
Spring barley 2001						
Triazinamin-methyl[1] (Express)	May 01	Jul 03	1941	951	10	<0.02
Flamprop-M-isopropyl (Barnon Plus 3)	Jun 01	Jul 03	1928	944	3	<0.01
- *flamprop (free acid)*						<0.01
Propiconazole (Tilt Top)	Jun 01	Jul 03	1928	944	3	<0.01
Fenpropimorph (Tilt Top)	Jun 01	Jul 03	1928	944	3	<0.01
- *fenpropimorphic acid*						<0.01
Dimethoate (Perfekthion 500 S)	Jul 01	Jul 03	1882	937	3	0.02
Maize 2002						
Glyphosate (Roundup Bio)	Oct 01	Apr 06	3802	1694	44	0.13
- *AMPA*						0.06
PHCP[2] (Lido 410 SC)	May 02	Jul 04	1764	738	6	0.06
Terbuthylazine (Lido 410 SC)	May 02	Apr 06	3320	1327	6	0.07
- *desethyl-terbuthylazine*		Apr 05				0.15
- *2- hydroxy-terbuthylazine*		Apr 05				[3]
- *2-hydroxy-desethyl-terbuthylazine*		Apr 05				[3]
- *desisopropyl-atrazine*		Apr 05				[3]
Peas 2003						
Bentazone (Basagran 480)	May 03	Jul 06	2634	1055	44	0.26
- *AIBA*						<0.01
Pendimethalin (Storm SC)	May 03	Apr 06	2634	1055	44	<0.01
Glyphosate (Roundup Bio)	Sep 03	Apr 06	2207	971	0	<0.01
- *AMBA*						0.02
Winter wheat 2004						
Prosulfocarb (Boxer EC)	Oct 03	Apr 06	2125	974	37	0.01
MCPA (Metaxon)	May 04	Jul 06	1797	710	4	<0.01
- *4-chlor,2-methylphenol*						<0.01
Azoxystrobin (Amistar)	Jun 04	Jul 06	1781	706	0	0.01
- *CyPM*		Jul 07	2931	1202	0	0.09
Pirimicarb (Pirimor G)	Jul 04	Jul 07	2818	1205	0	<0.01
- *Pirimicarb-desmethyl*						<0.01
- *Pirimicarb-desmethyl-formamido*						<0.02
Spring barley 2005						
Fluroxypyr (Starane 180 S)	May 05	Jul 07	2012	830	11	<0.02
Azoxystrobin (Amistar)	Jun 05	Jul 06	862	332	10	0.01
- *CyPM*	Jun 05	Jul 07	2012	828	10	0.02
Pirimicarb (Pirimor G)	Jul 05	Jul 07	1933	818	0	<0.01
- *Pirimicarb-desmethyl*						<0.01
- *Pirimicarb-desmethyl-formamido*						<0.01

Table A7.3 continued. Pesticides analysed at **Silstrup** with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C$_{mean}$ refers to average leachate concentration in the drainage water within the first drainage season after application. (See Appendix 2 for calculation methods).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C$_{mean}$ (µg/L)
Winter rape 2006						
Propyzamide (Kerb 500 SC)	Nov 05	Apr 08	2345	1115	75	0.22[4]
- RH-24644						0.01[4]
- RH-24580						<0.01[4]
- RH-24655						<0.01[4]
Clopyralid (Matrigon)	Apr 06	Apr 08	2009	859	8	<0.01

[1] *Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.*

[2] *Degradation product of pyridate. The parent compound degrades too rapidly to be detected by monitoring.*

[3] *Average leachate concentration within the first drainage season after application could not be calculated, as monitoring started January 2003 (7 months after application). See Kjær et al.(2007) for further information.*

[4] *Drainage runoff commenced two weeks prior to the application of propyzamide, and the weighted concentrations refer to the period from the date of application until 1 July 2007.*

Table A7.4. Pesticides analysed at **Estrup** with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application. (See Appendix 2 for calculation methods).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Spring barley 2000						
Metsulfuron-methyl (Ally)	May 00	Apr 03	2990	1456	29	<0.01
- triazinamin						<0.02
Flamprop-M-isopropyl (Barnon Plus 3)	May 00	Apr 03	2914	1434	2	0.02
- flamprop (free acid)						0.01
Propiconazole (Tilt Top)	Jun 00	Apr 05	4938	2294	0	0.01
Fenpropimorph (Tilt Top)	Jun 00	Jul 02	2211	1048	0	<0.01
- fenpropimorphic acid						<0.02
Dimethoate (Perfekthion 500 S)	Jun 00	Jul 02	2211	1048	0	<0.01
Pea 2001						
Glyphosate (Roundup Bio)	Oct 00	Jul 10[†]	10484	4977	123	0.54
- AMPA						0.17
Bentazone (Basagran 480)	May 01	Jul 08	7629	3621	9	0.03
- AIBA						<0.01
Pendimethalin (Stomp SC)	May 01	Jul 03	2208	1096	9	<0.01
Pirimicarb (Pirimor G)	Jun 01	Jul 05	4251	1995	10	0.01
- pirimicarb-desmethyl						<0.02
- pirimicarb-desmethyl-formamido						<0.02
Winter wheat 2002						
Ioxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	0.04[1]
Bromoxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	0.01[1]
Amidosulfuron (Gratil 75 WG)	Apr 02	Jul 04	2148	928	8	<0.01
MCPA (Metaxon)	May 02	Jul 04	2091	928	0	<0.01
- 4-chlor,2-methylphenol						<0.01
Propiconazole (Tilt 250 EC)	May 02	Apr 05	2920	1336	39	0.02
Pirimicarb (Pirimor G)	Jun 02	Jul 05	2982	1403	58	0.01
- pirimicarb-desmethyl						<0.02
- pirimicarb-desmethyl-formamido		Apr 06				<0.02
Fodder beet 2003						
Glyphosate (Roundup Bio)	Sep 02	Jul 10[†]	8289	3900	0	0.43
- AMPA						0.19
Ethofumesate (Betanal Optima)	May 03	Apr 06	2901	1371	50	0.11
Metamitron (Goltix WG)	May 03	Apr 06	2901	1371	50	1.1
- metamitron-desamino						0.21
Pirimicarb (Pirimor G)	Jul 03	Jul 05	2071	939	0	<0.01
- pirimicarb-desmethyl		Jul 05				<0.01
- pirimicarb-desmethyl-formamido		Apr 06				0.12
Spring barley 2004						
Fluroxypyr (Starane 180)	May 04	Jul 06	2073	1030	0	<0.02
Azoxystrobin (Amistar)	Jun 04	Jul 08	4452	2209	38	0.12
- CyPM						0.23
Maize 2005						
Terbuthylazine (Inter-Terbuthylazin)	May 05	Apr 09	4247	2042	32	0.48
- desethyl-terbuthylazine		Jul 09	4406	2051	32	0.31
- 2-hydroxy-terbuthylazine		Jul 08	3338	1628	32	0.11
- desisopropyl-atrazine		Apr 09	4247	2042	32	0.02
- 2-hydroxy-desethyl-terbuthylazine		Jul 08	3338	1628	32	0.24
Bentazone (Laddok TE)	Jun 05	Jul 08	3338	1628	10	0.18
- AIBA						<0.01
Glyphosate (Roundup Bio)	Nov 05	Jul 10[†]	5191	2460	68	4.04[1]
- AMPA						0.42[1]
Spring barley 2006						
Florasulam (Primus)	Jun 06	Jul 08	2442	1163	0	<0.01
- florasulam-desmethyl						<0.03
Azoxystrobin (Amistar)	Jun 06	Jul 08	2414	1170	0	0.03
- CyPM						0.13

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2006.

[1] Drainage runoff commenced about two and a half months prior to the application of ioxynil and bromoxynil, and the weighted concentrations refer to the period from the date of application until 1 July 2002.

Table A7.5. Pesticides analysed at **Faardrup** with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application (app. date) until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C$_{mean}$ refers to average leachate concentration in the drainage water the first drainage season after application. (See Appendix 2 for calculation methods).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C$_{mean}$ (µg/L)
Winter wheat 1999						
Glyphosate (Roundup 2000)	Aug 99	Apr 03	2526	947	0	<0.01
- AMPA						<0.01
Bromoxynil (Briotril)	Oct 99	Apr 02	1738	751	35	<0.01
Ioxynil (Briotril)	Oct 99	Apr 02	1738	751	35	<0.01
Fluroxypyr (Starane 180)	Apr 00	Apr 02	1408	494	7	<0.01
Propiconazole (Tilt Top)	May 00	Jul 03	2151	669	0	<0.01
Fenpropimorph (Tilt Top)	May 00	Jul 02	1518	491	0	<0.01
- fenpropimorphic acid						<0.01
Pirimicarb (Pirimor G)	Jun 00	Jul 03	2066	684	0	<0.01
- pirimicarb-desmethyl						<0.01
- pirimicarb-desmethyl-formamido						<0.02
Sugar beet 2001						
Glyphosate (Roundup 2000)	Oct 00	Jul 03	1747	709	0	<0.01
- AMPA						0.01
Metamitron (Goltix WG)	May 01	Jul 03	1512	507	4	0.01
- metamitron-desamino						0.01
Ethofumesate (Betanal Optima)	May 01	Jul 03	1512	507	4	0.06
Desmedipham (Betanal Optima)	May 01	Jul 03	1512	507	4	<0.01
- EHPC						<0.02
Phenmedipham (Betanal Optima)	May 01	Jul 03	1512	507	4	<0.01
- MHPC						<0.02
Fluazifop-P-butyl (Fusilade X-tra)	Jun 01	Jul 03	1460	503	0	<0.01
- fluazifop-P (free acid)						0.02
Pirimicarb (Pirimor G)	Jul 01	Jul 03	1460	503	1	<0.01
- pirimicarb-desmethyl						<0.01
- pirimicarb-desmethyl-formamido						<0.02
Spring barley 2002						
Flamprop-M-isopropyl (Barnon Plus 3)	May 02	Jul 04	1337	333	0	<0.01
- flamprop-M (free acid)						<0.01
MCPA (Metaxon)	May 02	Jul 04	1358	337	4	<0.01
- 4-chlor-2-methylphenol						<0.02
- triazinamin-methyl[1] (Express)	May 02	Jul 04	1358	337	4	<0.02
Dimethoate (Perfekthion 500 S)	Jun 02	Jul 04	1328	333	0	<0.01
Propiconazole (Tilt 250 EC)	Jun 02	Jul 04	1328	333	0	<0.01
Winter rape 2003						
Clomazone (Command CS)	Aug 02	Apr 05	1761	509	4	<0.02
- FMC65317 (propanamide-clomazon)						<0.02
Winter wheat 2004						
Prosulfocarb (Boxer EC)	Oct 03	Apr 06	1542	454	0	<0.01
MCPA (Metaxon)	Jun 04	Jul 06	1307	331	0	<0.01
- 4-chlor,2-methylphenol						<0.01
Azoxystrobin (Amistar)	Jun 04	Jul 07	2098	636	0	<0.01
- CyPM						<0.01
Maize 2005						
Terbuthylazine (Inter-Terbutylazin)	May 05	Jul 08	2078	666	4	0.67
- desethyl-terbuthylazine	May 05	Jul 08	2078	666		0.59
- 2-hydroxy-terbuthylazine	May 05	Jul 08	2078	666		0.04
- desisopropyl-atrazine	May 05	Jul 08	2078	666		0.03
- 2- hydroxy-desethyl-terbuthylazine	May 05	Jul 07	1428	465	4	0.07
Bentazone (Laddok TE)	May 05	Jul 07	1408	464	6	2.82
- AIBA						<0.01
Spring barley 2006						
Fluroxypyr (Starane 180 S)	May 06	Jul 08	1496	524	17	<0.02
Epoxiconazole (Opus)	Jun 06	Jul 08	1441	507	3	<0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
[1] *Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.*
† *Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2009.*

Appendix 8

New horizontal wells

New horizontal wells at each PLAP-site, with three new horizontal screens were established at each PLAP-site in 2011.

A horizontal well with three PE-screens (3 m long, separated by 1 m packer-section attached 0.8 m bentonite, slits of 0.1 mm, Figure A8.1) was installed September 2011 at all five PLAP-sites to optimize monitoring of the sites both in time and space.

The aim of the optimization was:

- at the sandy sites (Tylstrup and Jyndevad) to improve the early warning regarding pesticides and/or their degradation products leaching to the upper fluctuating groundwater by sampling a spatially representative sample of the porewater, which has just reaching the groundwater zone. The well was hence installed at 4.5 m depth at Tylstrup and 2.5 m depth at Jyndevad,

- at the loamy sites (Silstrup, Estrup and Faardrup) to improve spatial representativity of the water sampled in the variably saturated zone below drain-depth. To ensure this, the wells are (i) installed at 2 m depth, (ii) oriented such as it is as orthogonal to the orientation of the dominating fracture system as possible and at the same time crossing underneath a drain-line with one of its three filtersections/screens, and (iii) not affected by or affecting sampling from the vertical monitoring wells.

The location of the wells on the PLAP-fields is illustrated in Figure 2.1, 3.1, 4.1, 5.1 and 6.1. The wells/screens/filtersections are installed in boreholes of 9 cm in diameter. These boreholes are drilled by applying the directional drilling system RotamoleTM, which uses a dry percussion-hammer air pressure technique causing minimal disturbances of the soil medium.

Figure A8.1. Design of horizontal well with three filter sections of 3 m (inner diameter 25 mm; outer diameter 32 mm) each separated by 1m packer-section attached 0.8 m bentonite (thickness at installation 1 cm; expand to a thickness of 3.5 cm). Water can be sampled through two PE-tubes (inner diameter 4 mm; outer diameter 6 mm) ending 1 and 2 meters into each section, repectively.

Water sampling for pesticide analysis from these new horizontal screens started April 2012 (half a year after installation) and is only conducted when the soil media surrounding the screens is saturated. Water samples are, hence, collected at the:

- **Sandy sites** monthly. 3 liters are sampled from each filter via applying suction onto the two tubes. A half liter of the 3 liters, is passed through cells in a flow box measuring pH, temperature, and conductivity. The remaining 2½ liters is pooled with the equal volumes from the two other filters. Subsamples for analysis are then taken from the 7½ liter pooled sample.

- **Loamy sites** monthly if the groundwater table in the nearest vertical monitoring well is situated more than 20 cm above the screens. Having saturated conditions, one liter of water sample is collected from each screen via the two tubes during approximately 10 minutes. The liter sample is passed through cells in a flow box measuring pH, temperature, and conductivity. The samples from each screens are then pooled and send for analysis.

The design of the wells facilitates the possibility of collecting water from six points along the 12 m long well. This option is not utilised yet.